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KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES. XIV DISCUSSION OF RESULTS OF KINETIC MEASUREMENTS IN 80% AQUEOUS DIMETHYLSULFOXIDE

V. Nummert, M. Eek, and V. Palm

Laboratory of Chemical Kinetics and Catalysis, Tartu State University, Tartu Estonian SSR

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The results of kinetic measurements of the alkaline hydrolysis of substituted phenyl esters of p-toluenesulfonic acid in 80% (v/v) (50.3 M%) aqueous dimethylsulfoxide (DMSO), published before[1] were discussed.

The ρ^{o} values for the investigated reaction in 80% aqueous DMSO at 25, 50 and 75°C as well as the parameters of the Arrhenius equation for 3-chloro-, 3-nitro-, 4-nitro and unsubstituted phenyl tosylates were determined. It was shown using a program of multiple regression analysis, that in 80% aqueous DMSO as well as in water the reaction series investigated obeys the isoentropic relationship. It means that the dependence of free energy on the structure is completely connected with the corresponding changes in activation energy.

The values of changes $\Delta\rho^{o}_{S} = \rho^{o}_{S} - \rho^{o}_{H_2O}$ are in good accordance with the same values for the acidic dissociation of benzoic acids, anilinium ions as well as for the alkaline hydrolysis

of ethyl and phenyl benzoates.

In the previous papers[2-4], the dependence of the ρ^o values on the medium was thoroughly studied. It was found that in the case of various reactions considering m- and p-substituted benzene derivatives, when passing from one medium to another the ρ^o value changes by a constant $\Delta\rho^o$s, which is independent of the reaction studied. At the same time, it was found that the influence of the substituents dependent on the medium is caused mainly by the solvent electrophilicity[4].

In order to extend the study of ester hydrolysis kinetics involving the substituent effects dependence on the medium, the kinetics of the alkaline hydrolysis of substituted phenyl benzoates[5] and phenyl tosylates in 80% aqueous DMSO was investigated.

In the present paper, the results of kinetic measurements of the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X (X = 4-NO_2, 3-NO_2, 3-Cl, H) in 80% (v/v) (50.3 M%) aqueous DMSO at 25, 50 and 75°C published in previous paper[1] have been discussed.

The logarithmic values of the second order rate constants $k_2(1)$, $k_2(2)$ and k_2^o are given in Table 1.

The values of $k_2(1)$ and $k_2(2)$ were calculated according to equation (1)

$$k_1 = k_2 \cdot C_{OH^-} + \text{const} \qquad (1)$$

without taking into consideration the influence of electrolyte (alkali) concentration. When the $k_2(1)$ constants were calculated, the results of all parallel measurements at each hydroxide concentration were included, at the $k_2(2)$ constants calculation, the corresponding arithmetic means were embraced. The k_2^o values were obtained taking into account the influence of electrolyte (alkali) concentration according to the equation:

$$\log k_2' = \log k_2^o + B \cdot C_{OH^-} \qquad (2)$$

Table 1

Values of $\log k_2(1)$, $\log k_2(2)$ and $\log k_2^o$ for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X in 80% Aqueous DMSO

X	Temperature °C	$\log k_2(1)$	$\log k_2(2)$	$\log k_2^o$
H	25	-2.592±0.014	-2.588±0.015	-2.686±0.019
	50	-1.633±0.004	-1.620±0.013	-1.760±0.021
	75	-0.880±0.002	-0.860±0.003	-0.925±0.008
3-Cl	25	-1.321±0.003	-1.318±0.013	-1.448±0.010
	50	-0.561±0.002	-0.553±0.005	-0.714±0.017
	75	0.126±0.006	0.150±0.006	0.083±0.018
3-NO_2	25	-0.500±0.004	-0.503±0.009	-0.627±0.013
	50	0.229±0.003	0.233±0.002	0.165±0.008
	75	0.798±0.017	0.825±0.035	0.770±0.047
4-NO_2	25	-0.297±0.002	-0.303±0.002	-0.385±0.009
	50	0.391±0.009	0.394±0.010	0.315±0.017
	75	1.030±0.003	1.056±0.007	0.776±0.042
				1.030±0.003*
4-F	75	-0.573±0.005	-0.562±0.008	-0.558±0.009
4-CH_3	75	-1.169±0.008	-1.156±0.009	-1.216±0.007

* At calculations for 4-nitrophenyl tosylate at 75°C $k_2^o = k_2(1)$ was used.

where k_2^o is the second order rate constant for the infinitely diluted solution, k_2' - the same value for the hydroxide concentration considered:

One can see in Table 1 that the log $k_2(1)$ and log $k_2(2)$ values practically coincide. The log k_2^o values are, in general, for 0.1 - 0.17 logarithmic units smaller than the corresponding log k_2 values, without taking into consideration the influence of alkali concentration. The difference of log k_2^o - log k_2 is greater if the rate of reaction is slower and vice versa. The rate of the alkaline hydrolysis of 4-nitrophenyl tosylate at 75°C was measured at very low alkali concentrations and in the relationship between k_1 and C_{OH^-} the negative ordinate was observed[1]. The latter could be caused by uncertainty at the determination of alkali concentration. Therefore, the correction caused by alkali concentration in the case of 4-nitrophenyl tosylate exceeds the corresponding value for other pehnyl tosylates (difference log k_2^o - log $k_2(1)$ is equal to -0.254 logarithmic units), what apparently does not reflect the real situation. Consequently, in case of calculations including the k_2^o value for 4-nitrophenyl tosylate at 75°C the $k_2(1)$ constant, i.e. the value obtained without taking into consideration the influence of alkali concentration, was used. The rate of the alkaline hydrolysis of substituted phenyl tosylates increases considerably when passing from water to 80% (50.3 M%) aqueous DMSO. So, for example, the second order rate constant for unsubstituted derivative increases about 15 times at 75°C. A considerable increase in rate was also found in the case of alkaline hydrolysis of phenyl benzoates[5] and ethyl benzoates[6-8] during transition from water to 80% aqueous DMSO.

Increase in the rate of the alkaline hydrolysis of esters when passing from water to the aqueous DMSO could be considered as a result of the reduced OH^- ion solvation, as far as the existence of strong DMSO-water complexes was observed[7].

From rate constants $k_2(1)$, $k_2(2)$ and k_2^o for alkaline hydrolysis of phenyl tosylates in 80% aqueous DMSO the corresponding ρ^o values were found according to the equation

$$\log k^{X} = (\log k_o)_{calc} + \rho^o \sigma^o \qquad (3)$$

When calculating the recommended σ^o values from Tables[9] were used.

The results of such a data treatment are given in Table 2 (See Fig. 1).

Including the date of the alkaline hydrolysis of substituted phenyl benzoates, it was in the previous paper of this series shown that for several processes the ρ^o value increases by a constant when passing from water to 80 % aqueous DMSO. At 25°C.

$$\Delta\rho^o(50.3\ M\%\ DMSO) = \rho^o(50.3\ M\%\ DMSO) - \rho^o_{H_2O} = 0.787+0.081 \qquad (4)$$

The purpose of the present work was on the one hand, to check whether the relationship (4) is valid also in the case of the alkaline hydrolysis of substituted phenyl tosylates. On the other hand, the data of the alkaline hydrolysis of phenyl tosylates measured in a wide temperature range enables to study to what extent the ρ^o (50.3 M% DMSO) value depends on temperature.

Such a check was carried out by means of simple comparison of the ρ^o (50.3 M% DMSO) values at various temperatures as well as using the multilinear regression analysis in the corresponding co-ordinates.

The values of

$$\Delta\rho^o_s = \rho^o_{js} - \rho^o_{j(H_2O)} \qquad (5)$$

and $$\Delta\rho^o_s = a_{js} \cdot \rho^o_{j(H_2O)} \qquad (6)$$

for the alkaline hydrolysis of phenyl tosylates at 25, 50 and 75°C are given in Table 3. Index j denotes the reaction series, s is the medium. In the present case, s denotes 50.3 M% aqueous DMSO.

The values of a_{js} are determined according to the relationship (7)[15].

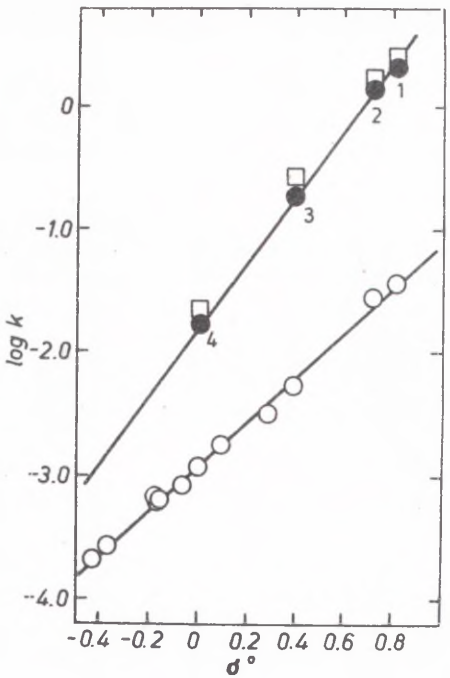

Fig. I. Relationship between log k and σ^{o} for alkaline hydrolysis of phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X at 50°C.

● - in 80% aqueous DMSO, $k = k_2^o$

□ - in 80% aqueous DMSO, $k = k_2(1)$,

○ - in water

X = 1. 4-NO_2; 2. 3-NO_2, 3. 3-Cl, 4. H.

Table 2

Values of ρ^{o} and $(\log k_o)_{calc}$ for Alkaline Hydrolysis of Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X in 80% Aqueous DMSO at 25, 50 and 75°C

Temperature °C	ρ^{o}	$(\log k_o)_{calc}$	s	r	n/n'
		Calculated from $k_2(1)$			
25	2.82 ± 0.20	-2.512±0.115	0.129	0.980	4/4
50	2.51 ± 0.14	-1.581±0.079	0.088	0.988	4/4
75	2.37 ± 0.14	-0.886±0.066	0.117	0.985	6/6
75	2.34 ± 0.08	-0.836±0.040	0.065	0.998	5/6
		Calculated from $k_2(2)$			
25	2.81 ± 0.21	-2.507±0.117	0.131	0.979	4/4
50	2.50 ± 0.14	-1.569±0.078	0.088	0.988	4/4
75	2.39 ± 0.14	-0.871±0.067	0.121	0.984	6/6
75	2.34 ± 0.02	-0.842±0.010	0.016	0.999	5/6
		Calculated from k_2^{o}			
25	2.82 ± 0.17	-2.618±0.097	0.108	0.985	4/4
50	2.60 ± 0.11	-1.727±0.063	0.070	0.993	4/4
75	2.40 ± 0.11	-0.921±0.053	0.094	0.991	6/6
75	2.38 ± 0.07	-0.883±0.036	0.059	0.996	5/6

Table 3

Values of $\Delta\rho_s^o = \rho_{js}^o - \rho_{j(H_2O)}^o$ for

Alkaline Hydrolysis of Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X

s = 50.3 M% DMSO

Temperature °C	$\rho_{H_2O}^o$	$\Delta\rho_s^o$ calculated from: $k_2(1)$	$k_2(2)$	k_2^o	$\Delta\rho_s^o = a_{js} \cdot \rho_{j(H_2O)}^o$ $k_2(1)$	$k_2(2)$	k_2^o	Notes
25	2.00	0.82	0.81	0.82	0.690	0.680	0.686	1)
50	1.85	0.66	0.65	0.75	0.545	0.535	0.632	2)
	1.80	0.71	0.70	0.80	0.531	0.520	0.616	
75	1.74	0.63	0.65	0.66	0.388	0.506	0.435	3)
		0.60	0.60	0.64	0.544	0.671	0.581	
	1.67	0.70	0.72	0.73	0.372	0.484	0.418	
		0.67	0.67	0.71	0.490	0.644	0.558	

1) Values of $\rho_{H_2O}^o$ found from relationship between $\rho_{H_2O}^o$ and temperature.

2) Values of $\rho_{H_2O}^o$ found from data in publications[10,11], including different number of substituents

3) Values of $\rho_{H_2O}^o$ found from data in publications [12,13], including different number of substituents.

$$\log k^{X}_{js} = (a_{js} + 1) \log k^{X}_{j(H_2O)} + b_{js} \qquad (7)$$

The results of such a data treatment are represented in Table 5. It also gives the values of

$$\Delta \log k^{X}_{js} = \log k^{X}_{js} - \log k^{X}_{j(H_2O)}, \qquad (8)$$

characterizing the changes of substituent effects when passing from water to 80% aqueous DMSO in case of the reaction series studied. It follows from the data given in Tables 2,3 and 5 that the susceptibility of the reaction series considered to the substituted phenyl inductive effect grows by 0.82 ρ^{o} units at 25°C and 0.66 units at 75°C, at an average 0.7 ρ^{o} units. So, $\Delta\rho^{o}_{s} = \Delta\rho^{o}$(50.3 M% DMSO) as the $\Delta \log k^{X}_{js}$ values decrease approximately only by 0.15 units when passing from 25°C to 75°C, while the $\Delta \log k^{X}_{js}$ value for unsubstituted derivative (X = H) does not practically depend on the temperature. At the same time, we cannot ignore the fact that the ρ^{o} value itself for the alkaline hydrolysis of phenyl tosylates in water as well as in 80% aqueous DMSO considerably depends on temperature, changing by 0.3 - - 0.45 units of ρ^{o} in the temperature range from 25°C to 75°C.

On the other hand, one must say that the $\Delta\rho^{o}_{s}$ values for the alkaline hydrolysis of substituted phenyl tosylates when passing from water to 80% aqueous DMSO in the range of the experimental error coincide with the $\Delta\rho^{o}_{s}$ values, determined from the data of the following other reaction series: the alkaline hydrolysis of phenyl and ethyl benzoates, acidic dissociation of benzoic acids and anilinium ions at 25°C. (Table 4).

For the reaction series presented above, the ρ^{o} (50.3 M% DMSO) values can actually be considered being constant. Between the ρ^{o}_{j} (50.3 M% DMSO) and $\rho^{o}_{j(H_2O)}$ values exist a linear relationship with the slope equal to one and the intercept equal to $\Delta\rho^{o}$(50.3 M% DMSO) (Fig. 2).

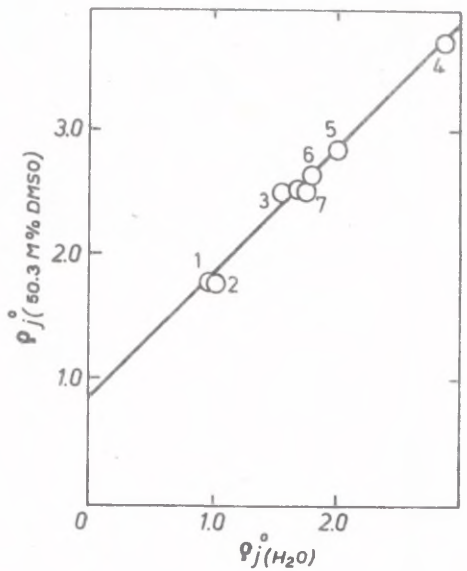

Fig. 2. Relationship between ρ°_{j}(50.3 M% DMSO) and $\rho^{\circ}_{j(H_2O)}$

1. Acidic dissociation of X-C_6H_5COOH at 25°C
2. Alkaline hydrolysis of $C_6H_5COOC_6H_4$-X at 25°C
3. Alkaline hydrolysis of X-$C_6H_4COOC_2H_5$ at 25°C
4. Acidic dissociation of X-$C_6H_4NH_3^+$ at 25°C
5. Alkaline hydrolysis of $CH_3C_6H_4SO_2OC_6H_4$-X at 25°C
6. The same reaction at 50°C
7. The same reaction at 75°C

$$\rho^{o}_{j}(50.3\ \text{M\% DMSO}) = (0.723 \pm 0.008) + (1.08 \pm 0.04)\ \rho^{o}_{j}(H_2O)$$

$n/n_o = 7/7$, $s = 0.085$, $r = 0.993$

In order to determine the change in the activation parameters when passing from water to the 50.3 M% aqueous DMSO, the E and log A parameters for 3-chloro-, 3-nitro-, 4-nitro- and unsubstituted phenyl tosylate were calculated from the dependence of the $k_2(1)$, $k_2(2)$, and k^{o}_{2} values on temperature (see Fig. 3). The corresponding E and log A values for 50.3 M% aqueous DMSO are presented in Table 6. For comparison, the E and log A values for the alkaline hydrolysis of substituted phenyl tosylates in water are given in Table 7.

Taking into consideration the alkali concentration according to equation (2) to some extent influences activation parameters E and log A. Without taking into account the salt effect, the decrease in the activation energy mainly leads to the medium effect when going from water to the 50.3 M% mixture of water and DMSO. The decrease in the activation energy for 4-nitrophenyl tosylate is nearly 2 kcal/mole but for the unsubstituted phenyl tosylate 0.5 kcal/mole, only. At the same time the increase in the preexponential is, on the average, 0.4 units. Taking into consideration the salt effect, a smaller decrease in the activation energy was observed, while log A increases about a unit (see Tables 6 and 7).

The relationships between E (kcal/mole) and σ^{o}_{x} could be described as follows (Fig. 4):

$$E(1) = (15.97 \pm 0.50) - (4.75 \pm 0.87)\ \sigma^{o}_{x} \qquad (9)$$
$$n/n_o = 4/4, \quad s = 0.553, \quad r = 0.865$$

$$E(2) = (16.11 \pm 0.50) - (4.55 \pm 0.88)\ \sigma^{o}_{x} \qquad (10)$$
$$n/n_o = 4/4, \quad s = 0.560, \quad r = 0.850$$

$$E(0) = (16.43 \pm 0.41) - (4.19 \pm 0.71)\ \sigma^{o}_{x} \qquad (11)$$
$$n/n_o = 4/4, \quad s = 0.452, \quad r = 0.883$$

where E(1), E(2) and E(0) are the activation energies calcu-

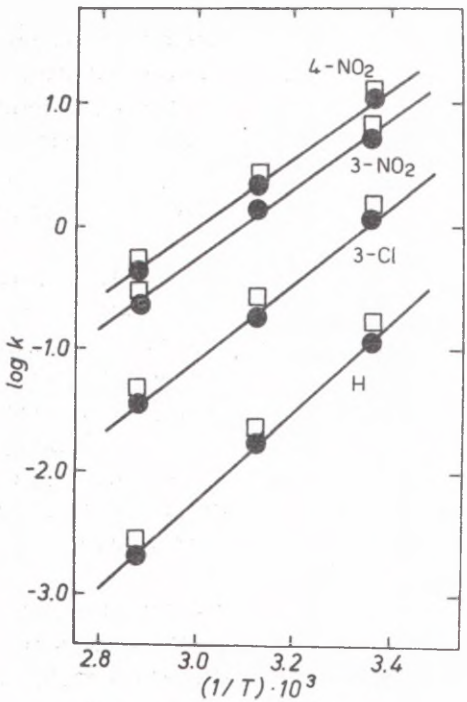

Fig. 3. Relationship between log k_2 and 1/T for alkaline hydrolysis of phenyl tosylates $CH_3C_6H_4SO_2C_6H_4$-X in 80% aqueous DMSO.

● - k_2^o

□ - $k_2(1)$

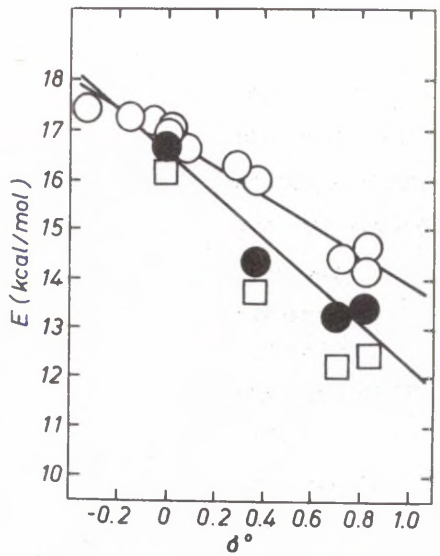

Fig. 4. Relationship between activation energy E and σ° for alkaline hydrolysis of $CH_3C_6H_4SO_2OC_6H_4$-X

○ - in water

● - in 80% DMSO, E = E(o).

□ - in 80% DMSO, E = E(1)

lated from the $k_2(1)$, $k_2(2)$ and k_2° constants, respectively. For water we have

$$E = (16.67 \pm 0.12) - (2.59 \pm 0.28)\,\sigma_x^{\circ} \qquad (12)$$

$$n/n_o = 13/13, \quad s = 0.262, \quad r = 0.912.$$

In water the alkaline hydrolysis of phenyl tosylates corresponds to the isoentropic reaction series. Taking into consideration the log A and E values calculated from the k_2° constants, a similar conclusion could be drawn for the alkaline hydrolysis phenyl tosylates in the 80% aqueous DMSO.

However, a more correct answer, in our opinion, to this

Table 4

Values of ρ°_{js} and $\Delta\rho^{\circ}_{js} = \rho^{\circ}_{js} - \rho^{\circ}_{j(H_2O)}$ for Various Reactions in 50.3 M% Aqueous DMSO

No	Reaction (a)	ρ°_{js}	$\rho^{\circ}_{j(H_2O)}$	$\Delta\rho^{\circ}_{js} = \rho^{\circ}_{js} - \rho^{\circ}_{j(H_2O)}$	Notes
1.	$C_6H_5COOC_6H_4 - X + OH^-$,	1.78±0.24	1.05±0.06	0.73	
	25°C (5)		1.02±0.08	0.76	
2.	$X\text{-}C_6H_4COOC_2H_5 + OH^-$,	2.35±0.06	1.52±0.006	0.83	32.0 M% DMSO
	25°C (1)	2.61±0.12		1.09	59.0 M% DMSO
		2.48		0.96	b)
3.	Acidic dissociation of	1.88±0.05	0.95±0.02	0.93	48.6 M% DMSO
	$X\text{-}C_6H_4COOH$, 25°C (1)	1.82±0.05		0.87	59.0 M% DMSO
		1.80		0.85	b)
		1.70		0.75	c)
4.	Acidic dissociation of	3.84±0.43	3.84±0.43	1.00	48.6 M% DMSO
	$X\text{-}C_6H_4NH_3^+$, 25°C (1)	3.72		0.88	b)

a) In brackets reference to the source of ρ° value is shown

Notes

b) The value of ρ°_j(50.3 M% DMSO) determined from the dependence of ρ°_j(M% DMSO) values on M% DMSO for binary mixture H_2O-DMSO

c) The values of ρ°_j (50.3 M% DMSO) determined from the dependence of ρ°_j(M% DMSO) values on M% DMSO for binary mixture H_2O-DMSO according to the data of Hojo and Utaka[23].

Table 5

Values of $\Delta \log k^{x}_{js} = \log k^{x}_{js} - \log k^{x}_{j(H_2O)}$ and Parameters of Equation $\log k^{x}_{js} = (a_{js} + 1) \log k^{x}_{j(H_2O)} + b_{js}$ for Alkaline Hydrolysis of Phenyl Tosylates

$CH_3C_6H_4SO_2OC_6H_4 - X$ (s = 50.3 M% Aqueous DMSO)

Temperature °C		$\log k^{x}_{j(H_2O)}$	$\Delta \log k^{x}_{js}$ from $k_2(1)$	$k_2(2)$	k^{o}_{2}	$a_{js} + 1$	b_{js}	s[d]	Notes
1	2	3	4	5	6	7	8	9	10
25	H	-3.890	1.298	1.302	1.204	1.345±0.130	2.761±0.407	0.180	1)
(a)	3-Cl	-3.193	1.872	1.875	1.648				
	3-NO_2	-2.378	1.878	1.875	1.751	1.340±0.140	2.743±0.411	0.181	2)
	4-NO_2	-2.247	1.950	1.944	1.862	1.343±0.127	2.643±0.377	0.167	3)
50	H	-2.917	1.284	1.297	1.157	1.295±0.103	2.253±0.220	0.127	1)
(b)	3-Cl	-2.290	1.729	1.737	1.576				
	3-NO_2	-1.532	1.761	1.765	1.697	1.289±0.103	2.247±0.219	0.127	2)
	4-NO_2	-1.417	1.808	1.811	1.802	1.342±0.079	2.243±0.167	0.0965	3)
75	4-CH_3	-2.360	1.190	1.204	1.144	1.223±0.277	1.660±0.436	0.417	1)
(c)	H	-2.090	1.210	1.230	1.165	1.313±0.222	1.938±0.120	0.109	
	4-F	-2.168	1.595	1.606	1.610				
	3-Cl	-1.507	1.633	1.657	1.590	1.291±0.301	1.817±0.475	0.455	2)
	3-NO_2	-0.839	1.637	1.664	1.609	1.250±0.264	1.674±0.0415	0.398	3)
	4-NO_2	-0.666	1.696	1.722	1.696	1.334±0.062	1.939±0.114	0.104	

Table 5 continued

a) Values of log $k^{x}_{j(H_2O)}$ at 25°C were calculated from the relationship between log k and temperature.

b) log $k^{x}_{j(H_2O)}$ values from papers[10,11]

c) log $k^{x}_{j(H_2O)}$ values from papers[12,13]

d) Standard error in case of data treatment by Eq.(7)

Notes

Values of a_{js} + 1 and b_{js}

1) calculated from $k_2(1)$
2) calculated from $k_2(2)$
3) calculated from k_2^o

Table 6

Values of E and log A for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X in 80% (50.3 M%) Aqueous DMSO

X	E(kcal/mole)	log A	s	r
	Calculated using $k_2(1)$			
H	16.27 ± 0.39	9.35 ± 0.27	0.029	0.997
3-Cl	13.72 ± 0.20	8.74 ± 0.14	0.015	0.999
3-NO_2	12.33 ± 0.32	8.55 ± 0.22	0.024	0.997
4-NO_2	12.58 ± 0.29	8.92 ± 0.19	0.021	0.998
	Calculated using $k_2(2)$			
H	16.42 ± 0.40	9.46 ± 0.27	0.030	0.997
3-Cl	13.92 ± 0.20	8.88 ± 0.19	0.020	0.998
3-No_2	12.62 ± 0.21	8.76 ± 0.15	0.016	0.999
4-NO_2	12.88 ± 0.38	9.13 ± 0.27	0.029	0.996
	Calculated using k_2^o			
H	16.88 ± 0.23	9.56 ± 0.16	0.017	0.999
3-Cl	14.46 ± 0.99	9.15 ± 0.67	0.074	0.970
3-NO_2	13.26 ± 0.42	9.12 ± 0.29	0.032	0.995
4-NO_2	13.40 ± 0.68	9.42 ± 0.46	0.051	0.988

Table 7

Values of E and log A for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X in Water *

X	E (kcal/mole)	log A	s	r	n/n_o
$4\text{-}NO_2$	14.31 ± 0.55	8.25 ± 0.41	0.077	0.991	7/7
	14.75 ± 0.24	8.57 ± 0.16	0.029	0.999	6/7
$3\text{-}NO_2$	14.42 ± 0.25	8.20 ± 0.17	0.030	0.999	6/6
3-Cl	16.02 ± 0.28	8.56 ± 0.18	0.020	0.999	5/5
4-Cl	16.49 ± 0.11	8.66 ± 0.15	0.025	0.999	5/5
$3\text{-}OCH_3$	16.60 ± 0.28	8.51 ± 0.19	0.031	0.999	5/5
H	16.41 ± 0.56	8.17 ± 0.37	0.040	0.995	5/5
	16.85 ± 0.31	8.47 ± 0.21	0.034	0.999	4/5
	17.00 ± 0.16	8.58 ± 0.11	0.020	0.999	6/6**
3-Me	17.25 ± 0.43	8.61 ± 0.28	0.022	0.998	4/4
$4\text{-}NH_2$	17.45 ± 1.00	8.25 ± 0.68	0.053	0.986	4/4
$3\text{-}NH_2$	16.28 ± 0.73	7.81 ± 0.48	0.044	0.992	4/4
	17.16 ± 0.50	8.31 ± 0.35	0.027	0.996	4/4***

* Date from papers[10-14] were used

** Values of log k_o calculated according to equation $\log k^x = \log k_o + \rho^o\sigma^o$ were used

*** Value of $k = 4.83 \cdot 10^{-3}$ at 75°C was used.

issue could give the common data processing according to equation (13)

$$\log k_T^x = \log k_0^o + C_x \sigma_x^o + C_T(1/T) + C_{xT}\sigma_x^o(1/T) \qquad (13)$$

including the data for various temperatures.

The expressions (14) and (15)

$$E^x = 2.3R(C_T + C_{xT}\sigma_x^o) \qquad (14)$$

$$\log A^x = \log k_0^o + C_x \sigma_x^o \qquad (15)$$

are valid for activation parameters. The slope of the relationship between E^x and σ_x^o is determined as $2,3\ R \cdot C_{xT}$.

The equation (13) could be rewritten as follows:[14]

$$\log k_T^x = \log k_0^o + C_T(1/T) + \left[C_x + C_{xT}(1/T)\right] \sigma_x^o \qquad (16)$$

where $$C_x + C_{xT}(1/T) = \rho^o T \qquad (17)$$

and $$\log k_T^o = \log k_0^o + C_T(1/T) \qquad (18)$$

In the case of isoentropic reaction series $C_x = 0$ and the isokinetic temperature is determined as ratio C_{xT}/C_x.

When simultaneously substituent temperature and medium are variable, the kinetic data can be in principle described by the following multilinear equation:

$$\log k_{TS}^x = \log k_{00}^o + C_x\sigma_x^o + C_T(1/T) + C_{xT}\sigma_x^o(1/T) + C_S \Delta S +$$

$$+ C_{ST}(1/T)\Delta S + C_{xS}\sigma_x^o \Delta S + C_{xCT}\sigma_x^o (1/T)\Delta S \qquad (19)$$

Accepting that

$$\log k^o_{TS} = \log k_{00}^o + C_T(1/T) + C_S \Delta S + C_{TS}(1/T)\Delta S \qquad (20)$$

one will obtain the following equation :

$$\log k^x_{TS} - \log k^o_{TS} = C_x\sigma_x^o + C_{xT}\sigma_x^o(1/T) + C_{xS}\sigma_x^o \Delta S +$$

$$+ C_{xTS}\sigma_x^o(1/T)\Delta S \qquad (21)$$

from which it follows that:

$$\rho^{o}_{TS} = C_x + C_{xT}(1/T) + C_{xS}\Delta S + C_{xTS}(1/T)\Delta S \qquad (22)$$

In medium S

$$E^{x}_{s} = 2.3\,R(C_T + C_{TS}\Delta S + C_{xT}\sigma'^{o}_{x} + C_{xTS}\,\sigma'^{o}_{x}\Delta S) \qquad (23)$$

and

$$\log A_o^{x} = \log k^{o}_{00} + C_x\sigma'^{o}_{x} + C_S\Delta S + C_{xS}\sigma'^{o}_{x}\Delta S \qquad (24)$$

In relationship (19), (21)-(23), the coefficient C_{xTS} characterizes the intensity of the simultaneous influence of temperature and medium on substituent effects.

At the data treatment

$\Delta S = \Delta E_S = E_S - E_{H_2O}$ was used where E_S is a parameter of electrophilicity (or general acidity)[15,16].

Besides water and 80% aqueous DMSO, the data for 30%, 60% and 80% aqueous ethanol[18,19] as well as the log k values for concentrated solutions of salts NaCl (4.84 M)[13] and $NaClO_4$ (5.3 M)[12] were embraced. For binary mixtures of water with ethanol the E values from publication[21] were used. The values of the electrophilicity parameter ΔE_S for the 80% aqueous DMSO were calculated from $\Delta\rho_s = 0.755$ for the acidic dissociation of benzoic acids according to equation[4]

$$\Delta\rho^{o}_{s} = \rho^{o}_{s} - \rho^{o}_{H_2O} = -0.0842\,(E_S - E_{H_2O}) \qquad (25)$$

The value of $\Delta\rho^{o}_{s} = 0.755$ was found from the linear relationship between the $\Delta\rho^{o}$ values for the acidic dissociation of benzoic acids and M% DMSO in binary mixture H_2O - DMSO: $\Delta\rho^{o} = 0.150.M\%$

At the data treatment including various media for the 80% aqueous DMSO, the k^{o}_{2} values were used.

For taking into account the influence of temperature the scale 1000/T was used.

The statistical data processing was carried out on a "Nord-100" computer using the program of multiple regression

analysis composed by one of the authors of the present paper*.

The program enables to treat data in four different ways:

1. Exclusion of insignificant argument scales was performed before excluding considerably deviating points.
2. Exclusion of significantly deviating points was performed before excluding insignificant argument scales.

Before exclusion significantly deviating points, only the insignificant scales which cause total nonorthogonality were excluded.

Both ways of data treatment have two different modes of forming cross terms:

1. Cross terms can be formed from centrated basic argument scales.
2. Cross terms are formed from non-centrated basic argument scales.

The results of phenyl tosylates data treatment according to equations (13) and (17) are given in Table 8. Both in water and in 80% aqueous DMSO, coefficient C_x either practically does not differ from zero or term $C_x\sigma_x^{o}{}^{x}$ was excluded as a result of data treatment**. It indicates to the fact that in the 80% aqueous DMSO, the reaction series considered corresponds to the isoentropic relationship. Coefficient C_T was found to be close to the same value for water, while the activation energy for unsubstituted compound just a little depends on the medium.

* Some fundamental principes of the algorithm used has been described previously [4,22].

** At the data treatment using cross terms formed from centrated basic argument scales term $C_x\sigma_x^{o}$ is significant but the recalculated C_x value does not practically differ from zero.

Table 8

Results of Data Treatment According to Equations (13) and (17)* for Alkaline Hydrolysis of Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4X$

	$\log k_o^o$	C_x	C_T	C_{xT}	s	n/n_o	t	Jk	Notes
1	2	3	4	5	6	7	8	9	10
				in 50.3 M% aqueous DMSO					
1.	9.44±0.39	-0.264±0.391	-3.599±0.126	0.921±0.354	0.077	12/14	0.99	1A	1)
2.	9.32±0.33	-	-3.560±0.106	0.836±0.021	0.073	12/14	0.99	1B	1)
3.	8.66±0.41	-	-3.322±0.136	0.828±0.026	0.099	12/14	0.99	1B	2)
4.	9.22±0.39	-0.384±0.363	-3.494±0.128	0.947±0.341	0.084	13/14	0.99	1A	3)
5.	9.06±0.35	-	-3.441±0.115	0.821±0.021	0.080	13/14	0.99	1B	3)
6.		-0.069±0.033		0.861±0.011	0.037	3/3	0.99	1B	6)
				in water					
7.	8.33±0.12	-0.048±0.041	-3.632±0.040	0.580±0.108	0.048	44/45	0.99	2A	4)
8.	8.34±0.12	-0.042±0.038	-3.636±0.038	0.583±0.104	0.046	42/45	0.95	2A	4)
9.	8.54±0.17	-0.158±0.358	-3.702±0.056	0.645±0.117	0.053	45/45		2B	4)
10.	8.37±0.12	-	-3.645±0.038	0.594±0.062	0.048	44/45	0.99	2B	4)
11.	3.89±0.11	-	-3.649±0.037	0.594±0.060	0.046	43/45	0.97	2B	4)
12.	8.31±0.11	0.023±0.029	-3.627±0.036	0.587±0.089	0.044	57/59	0.99	2A	5)

Table 8 continued

1	2	3	4	5	6	7	8	9	10
13.	8.36 ± 0.11	0.026 ± 0.027	-3.630 ± 0.035	0.587 ± 0.086	0.042	56/59	0.97	2A	5)
14.	8.20 ± 0.09	0.162 ± 0.021	-3.592 ± 0.031	0.547 ± 0.074	0.034	51/59	0.95	2A	5)
15.	8.56 ± 0.14	-0.276 ± 0.300	-3.707 ± 0.045	0.681 ± 0.098	0.052	59/59		2B	5)
16.	8.32 ± 0.10	-	-3.629 ± 0.033	0.594 ± 0.050	0.044	57/59	0.99	2B	5)
17.	8.33 ± 0.10	-	-3.632 ± 0.032	0.595 ± 0.049	0.042	56/59	0.97	2B	5)
18.	8.26 ± 0.08	-	-3.609 ± 0.027	0.600 ± 0.041	0.034	51/59	0.95	2B	5)
19.		-0.357 ± 0.170		0.709 ± 0.056	0.030	6/6	0.93	1B	6)

* n_o - Total number of data subjected to the data treatment

n - Number of points remained after excluding of significantly deviating points

t - Confidence level

Jk - Number "1" means that the procedure of exclusion of significantly deviating points is completed before the exclusion of insignificant argument scales. In the case of "2" the procedure is vice versa. When the letter "A" is added to numbers then the cross terms are formed as a product of centrated basic argument scales. In the case of letter "B" the cross terms are formed from noncentrated basic

"-" - a corresponding argument scale is excluded as insignificant during the data processing

Table 8 continued

Notes.

1. Calculated from k_2^o
2. Calculated from $k_2(1)$
3. Calculated from $k_2(2)$
4. Only those m- and p-substituted pehnyltosylates with uncharged substituents were included for which data in a wide temperature range are available (from 15 to 75 or 85°C).
5. All data for m- and p-substituted pehnyl tosylates with unchanged substituents are embraced
6. Calculated according to Eq. (17).

The dependence of the activation energy on the structure is characterized by coefficient C_{xT}, which in 80% aqueous DMSO is but a little higher than in water. In relationships between E_x and σ_x^o such a difference increases by 2.3 R times (see Eq. (9) - (12)).

In paper[4] at the investigation of the influence of the medium parameters on the substituent effects at the constant temperature the following equation was used

$$\log k^x_{js} - \log k^o_{js} = C_x \sigma_x^o + C_{xS} \sigma_x^o \qquad (26)$$

In order to check whether the equation of type (21) is valid when the simultaneous influence of temperature and medium on the substituent effects is considered the values of $\log k^x_{TS} - \log k^o_{TS}$ have been treated according to equations (19), (21) and (27).

$$\log k^x_{TS} - \log k^o_{TS} = C_x \sigma_x^o + C_{xT} \sigma_x^o (1/T) + C_{xTS} \sigma_x^o (1/T) \Delta S$$

Results of such data treatment are given in Tables 9 and 10.

When $\Delta \log k^x_{TS} = \log k^x_{TS} - \log k^o_{TS}$, in data treatment according to equation (19) where $\log k^x_{TS} = \Delta \log k^x_{TS}$ one will obtain

$$\log k^x_{TS} - \log k^o_{TS} = (-0.197 \pm 0.043)\, \sigma_x^o + (0.073 \pm 0.017)\, \Delta E + (0.651 \pm 0.113) \sigma_x^o (1/T) - (0.0833 \pm 0.0043) \sigma_x^o \Delta E - (0.0258 \pm 0.0109)(1/T)\, \Delta E \qquad (28)$$

$$t = 0.95, \quad n/n_o = 65/72, \quad s = 0.057$$

Term $C_{xTS} \sigma_x^o (1/T) \Delta E$ is excluded during data treatment. It shows that the simultaneous influence of temperature and medium on substituent effects could be considered as insignificant, though the ρ^o values tend to decrease at higher temperatures (see Table 3). The $\log k^o_{00}$ value and coefficient C_x are indisquishable from zero. The C_x value differs from zero if the cross terms are used formed from centrated

basic argument scales. When the cross terms are formed from the noncentrated argument scales, the $C_x\sigma_x^{\circ}$ term is excluded as insignificant.

The values of C_S and C_{ST} coefficients show that the C_x and C_{ST} $(1/T)\Delta E$ terms compensate each other and the sum $C_S\Delta E + C_{ST}(1/T)\Delta E$ practically does not differ from zero. This also gives evidence about the validity of the relationship like (21).

On the other hand, the values of coefficients C_T, C_S and C_{xS} show that in case of the media considered, the log A value only slightly depends on the substituent:

$$\log A = -0.197\,\sigma_x^{\circ} + 0.073\Delta E - 0.0833\,\sigma_x^{\circ}\cdot\Delta E$$

To the isoentropic relationship corresponds entirely the result of data treatment according to equations (21) and (27) (see Tables 9 and 10).

$$\log k^x_{TS} = \log k^x_{TS} - \log k^{\circ}_{TS} = (0.588\pm0.005)\,\sigma_x^{\circ}(1/T) -$$

$$- (0.0298\pm0.0010)\,\sigma_x^{\circ}(1/T)\Delta E \qquad (29)$$

at $t = 0.95$, $n/n_o = 66/72$, $s = 0.060$.

The overall treatment of the log k values for the alkaline hydrolysis of phenyl tosylates in various media according to equation (19) could be considered rather carefully. It was found that when the medium electrophilicity decreases, the ρ° value, i.e. the susceptibility to the substituent effects grows[4]. When passing from water to the 80% DMSO, the log k_o value increases similarly to the ρ° value, but when passing from water aqueous-alcohol solutions, the ρ° value grows but the log k_x value for the unsubstituted compound decreases.[17,18] Including the data for water and the 80% aqueous DMSO at various temperatures, equation (19) has also two possible versions, like in the case of the $\Delta\log k^x_{TS}$ values[1] treatment.

If at the data treatment the cross terms are formed from noncentrated scales, (version of data treatment "1B", see Table 8).

Table 9

Results of the log k^{x}_{TS} - log k^{o}_{TS} Values Treatment According to Equations (19), (21) and (27) for Alkaline Hydrolysis of Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X.

		Jk*	C_x	C_T	C_S	C_{xT}	C_{xS}	C_{ST}	C_{xTS}
1	2	3	4	5	6	7	8	9	10
1.	(19)	1A and 2A	-0.155± ±0.056	0.043± ±0.049	0.102±0.020	0.638±0.131	-0.0855± ±0.0049	-0.0351± ±0.0122	-
2.	(19)	1A and 2A	-0.197± ±0.043	0.078± ±0.045	0.073±0.017	0.651±0.113	-0.0833± ±0.0043	-0.0258± ±0.0109	-
3.	(19)	1B and 2B	-	-	0.121±0.032	0.586±0.060	-0.0853± ±0.0048	-0.0415± ±0.0109	-
4.	(21)	1B	-0.406± ±0.367			0.729±0.122	-0.0247± ±0.0768		-0.0384± ±0.0254
5.	(21)	1B	-			0.587±0.006	-		-0.0302± ±0.0011
6.	(21)	1B	-			0.589±0.006	-		-0.0303± ±0.0010
7.	(21)	1B	-			0.588±0.006	-		-0.0298± ±0.0010

Table 9 continued

1	2	3	4	5	6	7	8	9	10
8.	(27)	1B	$-0.558\pm$ ± 0.328			0.746 ± 0.109			$-0.0302\pm$ ± 0.0014
9.	(27)	1B	-			0.587 ± 0.006			$-0.0302\pm$ ± 0.0011
10.	(27)	1B	-			0.589 ± 0.006			$-0.0303\pm$ ± 0.0010
11.	(27)	1B	-			0.588 ± 0.005			$-0.0298\pm$ ± 0.0010

* See notes to Table 8

Table 10

Results of the log k^{x}_{TS} - log k^{o}_{TS} Data Treatment According to Equations (19) , (21) and (27) for Alkaline Hydrolysis of Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X

		Jk		log k^{o}_{oo}	s	n/n_o	t	Notes
1.	(19)	1A	2A	-0.132±0.146	0.066	70/72	0.99	
2.	(19)	1A	2A	-0.236±0.134	0.057	65/72	0.95	
3.	(19)	1B	2B	-	0.065	70/72	0.99	
4.	(21)	1B		-0.015±0.013	0.086	72/72	-	1)
5.	(21)	1B		-	0.065	69/72	0.99	
6.	(21)	1B		-	0.062	67/72	0.97	
7.	(21)	1B		-	0.060	66/72	0.95	
8.	(27)	1B		-0.015±0.013	0.086	72/72	-	1)
9.	(27)	1B		-	0.065	69/72	0.99	
10.	(27)	1B		-	0.061	67/72	0.97	
11.	(27)	1B		-	0.060	66/72	0.95	

Notes

1) Results of the first solution - run.

$$\log k^{X}_{TS} = (8.35\pm0.10) - (3.639\pm0.034)(1/T) -$$
$$- (0.131\pm0.003)\Delta E + (0.594\pm0.006)\sigma_x^{\circ}(1/T) -$$
$$- (0.0280\pm0.0017)\sigma_x^{\circ}(1/T)\Delta E \qquad (30)$$

at $t = 0.95$, $n/n_o = 53/59$, $s = 0.046$

Terms $C_X \sigma_x^{\circ}$, $C_{TS}(1/T)\Delta E$, and $C_{xS}\sigma_x^{\circ}\Delta E$ were excluded during the data treatment.

If at the data treatment the cross terms are formed from the centrated basic argument scales (version "1A" for data treatment, see Table 8), then we obtain

$$\log k^{X}_{TS} = (8.44\pm0.11) - (3.667\pm0.037)(1/T) -$$
$$- (0.376\pm0.035)\sigma_x^{\circ} - (0.133\pm0.002)\Delta E +$$
$$+ (0.717\pm0.098)\sigma_x^{\circ}(1/T) - (0.085\pm0.0056)\sigma_x^{\circ}\Delta E \qquad (31)$$

at $t = 0.99$, $n/n_o = 55/59$, $s = 0.050$

Terms $C_{TS}(1/T)\Delta E$ and $C_{xTS}\sigma_x^{\circ}(1/T)\Delta E$ were excluded during the data treatment.

If the data for water, the 80% aqueous DMSO and the solutions of concentrated salts NaCl and $NaClO_4$ are subjected to the overall data treatment, the data for the salts solutions are excluded and the final result is analogous to the equations (30) and (31).

Equation (30) describes well the simultaneous influence of medium, temperature and substituents when passing from water to the 80% aqueous DMSO. In the case of isoentropic reaction series, terms $C_x\sigma_x^{\circ}$ and $C_{xS}\sigma_x^{\circ}\Delta S$ do not differ from zero. It was also found that when passing from water to 80% DMSO the $\log k_s^o - \log k_{H_2O}^o$ values for unsubstituted derivative do not depend on temperature (see Table 5), and in equation (19), term $C_{TS}(1/T)\Delta S$ was excluded during data treatment. (see Eq. 30).

References

1. N. Nummert and M. Eek, Organic Reactivity, 21, 304 (1984).
2. V. Nummert and V. Palm, Organic Reactivity, 17, 292 (1980).
3. V. Nummert and V. Palm, Organic Reactivity, 17, 333 (1980).
4. V. Nummert, Organic Reactivity, 18, 274(1981).
5. V. Nummert, M. Eek, and M. Piirsalu, Organic Reactivity, 18, 363 (1984).
6. E. Tommila and I. Palenius, Acta Chem. Scand., 17, 1980 (1963).
7. D. Roberts, J. Org. Chem. 30, 3516 (1965).
8. M. Hojo, M. Utaka, and Z. Yoshida, Tetrahedron Letters, 1, 25 (1966).
9. Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions, Vol. 5 (II), Moscow, 1979.
10. V. Maremäe and V. Palm, Reakts. sposobn. organ. soedin., 1,(2), 86 (1964).
11. V. Maremäe and T. Püssa, Reakts. sposobn. organ.soedin., 6, 732 (1969).
12. V. Nummert, M. Piirsalu, and I. Alakivi, Organic Reactivity, 15, 133 (1978)
13. V. Nummert and M. Piirsalu, Organic Reactivity, 19, 67 (1982).
14. V. Maremäe and V. Palm, Reakts. sposobn. organ. soedin., 11, 209 (1965).
15. V. Nummert, Organic Reactivity, 15, 412 (1978).
16. I. Koppel and A. Paju, Organic Reactivity, 11, 137 (1974).
17. V. Palm "Fundamentals of Quantitative Theory of Organic Reactions," "Khimiya," 2,1977.
18. V. Maremäe and J. Asenbusch, Reakts. sposobn. organ. soedin., 2, (1), 83 (1965).

19. V. Maremäe and V. Palm, Reakts. sposobn. organ. soedin., 3,(5), 192 (1965).
20. I. Koppel and J. Koppel, Organic Reaktivity, 15, 56 (1978).
21. V. Nummert, R. Pärismaa, and M. Piirsalu, Organic Reactivity, 21, 83 (1984).
22. A. Uri, A. Tuulmets, and V. Palm, Organic Reactivity, 20, 122 (1983).
23. M. Hojo, M. Utaka, and Z. Yoshida, J. Chem. Soc. Jap. Ind. Chem. Soc., 69, 885 (1966).

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CALCULATION OF IONIZATION POTENTIAL ACCORDING TO THE NUMBER OF INTERACTIONS BETWEEN STRUCTURAL UNITS 4. ALKENES AND CYCLOALKENES

P.K. Põldoja and T.F. Viik
Institute of Physics of the Estonian Academy of Sciences,
202400 Tartu, Estonian SSR

Institute of Astrophysics and Atmospheric Physics of
the Estonian Academy of Sciences,
202444 Tõravere, Estonian SSR

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Two new multiparametric methods are proposed to describe the first ionization potential (IP) of alkenes and cycloalkenes, within the frames of which it is possible to give a correct quantitative estimate for the effect of saturation" in the decrease of the first IP under the action of several alkyl substituents.

The first method describes the linear dependence of the IP of ethylene with several alkyl substituents on the arithmetic mean of the IPs of monosubstituted ethylenes.

The second method states that the changes in IP can be represented by an additive scheme of the contributions of the influence of characteristic groupings (structures).

The first ionization potential (IP) of alkenes is described by the energy of removing a π-electron of the C=C group.

The experimental measurements of the adiabatic IP have been carried out by a number of authors by using photoionization (PI) [1-4] and photoelectron spectroscopy (PES) [5-8]. Alkenes and cycloalkenes are being systematically studied mainly in two laboratories - at Paris University [5] and at the Institute of Physics of the Estonian Academy of Sciences in Tartu [2-3].

We know the IP values for 121 compounds (altogether there are 163 individual determinations - Table 1). Since the first IPs of cyklenes (starting from cyclopentenes) practically coincide with those of the alkenes with the same number of carbon atoms in respective positions [9], it has been taken into account in the systematization of compounds in Table 1. The mean accuracy of experimental data is about 0.02 eV.

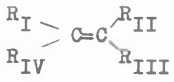
The influence of methyl groups on the value of IP has been studied theoretically in papers [12,13]. The pseudo-π-orbital of the methyl group conjugates with the π-orbital of the double bond (hyperconjugation). This explains the large change of the IP of ethylene caused by the substitution of hydrogen atoms by methyl groups. Such an influence has been noticed in the case of larger distances as well, since the methyl group imbedded into butadiene in position 2, interacts not only with the nearest double bond [13].

On the other hand, the radical-cation is well stabilized owing to the electron-donor ability of alkyl groups, the influence being transferred by charge delocalization [10].

In the correlation analysis of the first IP it is necessary to take into account the influence of inductive and resonance constants, the polarizability and number of hydrogen atoms in two neighbouring positions relative to the ionization center [14]. For the correlational calculations of IP the internal parameters have been used [15]. The empirical method of describing the IPs of aromatic compounds as the dependence on the number of Kekule-structures is known [16].

Table 1

Values of the First Adiabatic Ionization Potential (eV) for Alkenes and Cycloalkenes



$H_IHC{=}CH_2$

1. 0,0,0,0 10.517;10.517; 10.515[5];10.515[1]; 10.514;10.514; 10.51;10.51;10.51; 10.51;10.51;10.507; 10.51[7]
2. 1,0,0,0 9.744[5];9.74[6]; 9.73[1];9.73[7];9.73; 9.72.
3. 2,0,0,0 9.625[5];9.61; 9.59[7].
4. 3,0,0,0 9.524[5];9.50[1]; 9.50;9.50.
5. i3,0,0,0 9.533[5];9.51[1].
6. 4,0,0,0 9.478[5];9.46[1]; 9.45.
7. i4,0,0,0 9.452[5].
8. t4,0,0,0 9.450[5].
9. 5,0,0,0 9.442[5].
10. neo5,0,0,0 9.399[5].
11. 6,0,0,0 9.427[2].
12. 7,0,0,0 9.42[2].
13. 8,0,0,0 9.417[2].

$R_IR_{IV}C{=}CH_2$

14. 1,0,0,1 9.239[5];9.23[1]; 9.23[4].
15. 1,0,0,2 9.148[5];9.12[1].
16. 1,0,0,3 9.076[5].
17. 1,0,0,i3 9.072[5].
18. 1,0,0,4 9.039[5].
19. 1,0,0,i4 9.025[5].
20. 1,0,0,t4 9.016[5].
21. 1,0,0,neo5 8.909[5].
22. 2,0,0,2 9.061[5].
23. t4,0,0,t4 8.795[5].

$R_IHC{=}CR_{II}H$

24. 1,1,0,0 9.13[1];9.13[4]; 9.124[5];9.11[7].
25. 1,2,0,0 9.036[5].

Table 1 continued

26. 1,2,0,0  9.02[3]

27. 1,3,0,0 8.969[5].

28. 1,i3,0,0 8.976[5].

29. 1,i4,0,0 8.917[5].

30. 1,t4,0,0 8.922[5].

31. 1,5,0,0 8.913[2].

32. 1,6,0,0 8.90[2].

33. 1,7 0,0 8.899[2].

34. 2,2,0,0 8.954[5].

35. 2,2,0,0  8.94[3].

36. 2,2,0,0  8.95[3].

37. 2,3,0.0 8.87[8].

38. 2,3,0,0  8.91[3].

39. 2,3,0,0  8.88[3].

40. 2,i3,0,0  8.89[3].

41. 2,4,0,0 8.849[5];8.859[2].

42. 2,4,0,0  8.88[3].

43. 2,4,0,0 8.84[3].

44. 2,i4,0,0  8.81[3].

45. 2,s4,0,0  8.83[3].

46. 2,5,0,0 8.84[2].

47. 2,5,0,0  8.83[3].

48. 2,CH(CH$_3$)C$_3$H$_7$,0,0

 8.80[3].

49. 2,6,0,0 8.832[2].

 8.85[3].

51. 2,6,0,0  8.84[3].

52. 2,CH(CH$_3$)C$_4$H$_9$,0,0

 8.80[3].

53. 2,CH(CH$_3$)iC$_4$H$_9$,0,0

 8.77[3].

54. 2,CH(CH$_3$)sC$_4$H$_9$,0,0

 8.74[3].

55. 2,i6,0,0  8.83[3].

56. 2,7,0,0  8.84[3].

57. 2,CH(CH$_3$)C$_6$H$_{13}$,0,0

 8.78[3].

Table 1 continued

58. 2,$CH(CH_3)C_7H_{15}$,0,0

8.78[3].

59. 3,3,0,0 8.841[5];8.836[2].

60. 3,3,0,0  8.82[8].

61. i3,i3,0,0, 8.846[5].

62. 3,4,0,0 8.801[2].

63. 3,5,0,0 8.784[2].

64. 4,4,0,0 8.773[2];8.766[5].

65. 4,4,0,0  8.80[8].

66. t4,t4,0,0 8.695[5].

$R_IHC{=}CHR_{III}$

67. 1,0,1,0 9.13[1];9.13[4]; 9.122[5];9.10[7].

68. 1,0,2,0 9.036[5].

69. 1,0,3,0 8.966[5].

70. 1,0,i3,0 8.972[5].

71. 1,0,i4,0 8.919[5].

72. 1,0,s4,0 8.912[5]

73. 1,0,t4,0 8.908[5].

74. 1,0,5,0 8.913[2].

75. 1,0,6,0 8.900[2].

76. 1,0,7,0 8.903[2].

77. 2,0,2,0 8.965[5].

78. 2,0,4,0 8.854[2].

79. 2,0,5,0 8.84[2].

80. 2,0,6,0 8.83[2].

81. 3,0,3,0 8.836[2];8.830[5].

82. i3,0,i3,0 8.838[5].

83. 3,0,4,0 8.809[2].

84. 3,0,5,0 8.782[2].

85. 4,0,4,0 8.762[2];8.760[5].

86. t4,0,t4,0 8.741[5].

$R_IHC{=}CR_{II}R_{III}$

87. 1,1,1,0 8.682[5];8.68[4].

88. 1,2,1,0  8.60[3].

89. 1,2,2,0  8.53[3].

90. 1,2,3,0  8.48[3].

91. 1,2,4,0  8.45[3].

92. 1,2,5,0  8.45[3].

93. 1,2,6,0  8.43[3].

94. 1,2,7,0  8.41[3].

95. 1,2,i4,0  8.44[3].

96. 1,2,i5,0  8.44[3].

Table 1 continued

$R_IR_{IV}C{=}CR_{II}R_{III}$

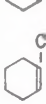
97. 2,2,2,0 — 8.480[5].

98. 2,2,2,0 — 8.48[3].

99. 2,2,3,0 — 8.43[3].

100. 2,2,4,0 — 8.41[3].

101. 2,2,5,0 — 8.37[3].



102. 2,2,6,0 — 8.37[3].

103. 2,2,7,0 — 8.37[3].

104. 2,2,i4,0 — 8.40[3].

105. t4,neo5,1,0 — 8.346[5].

106. i3,t4,t4,0 — 8.307[5].

107. t4,t4,t4,0 — 8.169[5].

108. 1,1,1,1 — 8.30[4];8.271[5];8.26[6].

109. 2,1,1,1 — 8.213[5].

110. 3,1,1,1 — 8.186[5].

111. i3,1,1,1 — 8.165[5].

112. 4,1,1,1 — 8.145[5].

113. 5,1,1,1 — 8.132[5].

114. neo5,1,1,1 — 8.097[5].

115. 2,1,1,2 — 8.170[5].

116. 2,2,1,1 — 8.172[5].

117. 2,1,2,1 — 8.156[5].

118. 2,2,2,1 — 8.128[5].

119. 3,1,2,1 — 8.077[5].

120. 4,1,1,2 — 8.101[5].

121. 3,2,2,2 — 8.041[5].

Comments. In this table after the number of compound the abbreviated formula is given in which the four substituents R_I, R_{II}, R_{III} and R_{IV} are represented in turn. The substituents are marked as follows: H-0, CH_3-1, C_2H_5-2, H-C_3H_7-3, iso-C_3H_7-i3 etc. References are given for important series only, the results for other series are taken from papers [10, 11].

In paper [5], the influence of the number of carbon atoms in alkyl substituents and the influence of the number of substituents on the first IP of alkenes are discussed. When the number of substituents is growing, we can observe the effect of saturation in the change of IP, i.e. there are deviations from additivity. It is shown that the IP of alkenes with several alkyl groups depends linearly on the IPs of multisubstituted alkenes, if there is one common variable alkyl group and other groups are fixed. We do not know any universal methods of calculating the IPs of all alkenes which could give accuracy close to experimental.

In our previous papers, a method parameterizing the changes of the IP of alkynes [17] and aldehyde-ketones [18] is described. This method takes into account the formal interactions between structural units and the centre of ionization, and between each other. In the present paper, a quantitative description of the first IPs of alkenes and cycloalkenes is given by using two methods of internal parameterizing [15,17,18].

The IP of alkenes with four alkyl substituents $R_IR_{IV}C=CR_{II}R_{III}$ (where R_I, R_{II}, etc are the alkyls groups) can be described by using the IPs of the monosubstituted compunds as follows:

$$I = a_o + a_1 \left[(I_{R_IHC=CH_2} - I_{CH_3HC=CH_2}) + (I_{R_{II}HC=CH_2} - I_{CH_3HC=CH_2}) + \right.$$

$$\left. + (I_{R_{III}HC=CH_2} - I_{CH_3HC=CH_2}) + (I_{R_{IV}HC=CH_2} - I_{CH_3HC=CH_2}) \right] . \quad (1)$$

If there are only three (or two) alkyl substituents in the aforesaid compounds then the last term (or the two last terms) in square brackets must be omitted.

In order to describe all the alkenes or cycloalkenes we need five different forms of Eq. (1).

The coefficients a_o, a_1 and the statistical parameters of Eq. (1) for those five forms are given in Table 2.

Table 2

Coefficients and Statistical Parameters of Equation (1)

Type of alkenes No according to Table 1	a_0	a_1	n	M	s	r
$R_IR_{IV}C{=}CH_2$ (14-23)	9.232±0.010	0.763±0.037	10	13	0.021	0.987
$R_IHC{=}CR_{II}H$ (24-44,46-47,49-51,56,59-66)	9.116±0.006	0.660±0.015	35	41	0.014	0.994
$R_IHC{=}CHR_{III}$ (67-71,73-86)	9.116±0.004	0.655±0.010	19	24	0.009	0.997
$R_IHC{=}CR_{II}R_{III}$ (87-95,97-101,104-107)	8.661±0.012	0.514±0.024	18	18	0.021	0.984
$R_IR_{IV}C{=}CR_{II}R_{III}$ (108-121)	8.262±0.011	0.419±0.036	14	14	0.017	0.959

Comments. n - number of compounds; M - number of the values of the first IP; s - standard deviation; r - correlation coefficient.

As it can be seen in Table 1, cis- and trans-substitution are equivalent since the coefficients for the respective equations coincide. The larger the number of substituents, the weaker is their influence on the first IP, as the values of coefficients a_1 clearly show.

A simple transformation of Eq. (1) gives us a dependence of IP on the arithmetic mean of the first IPs of monoalkyl alkenes. We obtain the following equations, which are very handy for practical application.

For compounds of the type $R_I R_{IV} C{=}CH_2$:

$$I = -5.633 + 1.526\bar{I} \ , \qquad (2)$$

where

$$\bar{I} = (I_{R_I HC{=}CH_2} + I_{R_{IV} HC{=}CH_2})/2 \ ;$$

for cis-alkenes $R_I HC{=}CR_{II} H$:

$$I = -3.746 + 1.320\bar{I} \ ; \qquad (3)$$

for trans-alkenes $R_I HC{=}CHR_{III}$:

$$I = -3.650 + 1.310\bar{I} \ ; \qquad (4)$$

for alkenes of the type $R_I HC{=}CR_{II} R_{III}$:

$$I = -6.378 + 1.543\bar{I} \ ; \qquad (5)$$

for alkenes of the type $R_I R_{IV} C{=}CR_{II} R_{III}$:

$$I = -8.122 + 1.681\bar{I} \ . \qquad (6)$$

In Eqs. (5) and (6) $\bar{I}$ is the arithmetic mean of three or four IP values, respectively.

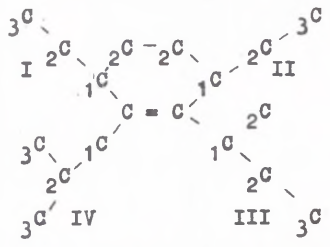
In addition to alkenes Eq. (1) describes substituted cycloalkenes in Table 1 as well. Their aliphatic correspondences are given before the structural formulas in Table 1.

All the values of the IP of 121 alkenes and cycloalkenes, represented in Table 1, are described by Eq. (7) with 14 parameters, which is based on the ideas of papers [17,18]

$$I = a_0x_0+a_1x_1+a_2x_2+ \ldots +a_{13}x_{13} . \qquad (7)$$

The regressors x_i of Eq. (7) are determined by the numbers of characteristic groupings in alkenes and they are given in Table 3. Such a definition of regressors reflects the essence of the method better than the one given previously [17,18] which used the number of formal interactions.

The designation of the positions of carbon atoms relative to the group C=C in alkenes and cycloalkenes is given in the figure. The basic idea of this additive method of calculation according to Eq.(7) is the assumption that the influence of each particular interaction in simple and complicated compounds is equal. For each grouping, in which there are additional interactions, the respective contribution to the change of the first IP is calculated.



The more complicated the compound is, the bigger is the number of the grouping, which arise due to branching and increase of substituents in long chains.

The regressors x_1-x_7 are given by the number of normal chains with various lengths around the group C=C or, in other words, the regressors x_1-x_7 are given by the number of carbon atoms in positions 1, 2, 3, ... 7 (see the figure). The regressors x_8+x_{12} describe the interactions between the substituents: x_8 - gem-interaction, x_9 and x_{12} - cis- and trans-interaction, the additional three- and fourfold interactions are given by the regressors x_{10} and x_{11} and the regressor x_{13} describes the number of α -branching. As an example a set of regressors for some alkenes is given in

Table 3

Regressors and Values for Coefficients of Equation (7)

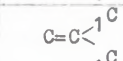
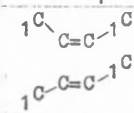
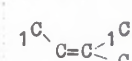
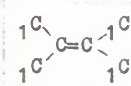
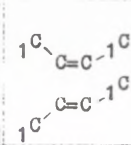
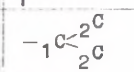
Regressors	Grouping	Coefficients	s
x_0	C=C	$a_0=10.512\pm0.006$	
x_1	C=C–$_1$C	$a_1=-0.822\pm0.008$	
x_2	C=C–$_1$C–$_2$C	$a_2=-0.098\pm0.004$	
x_3	C=C–$_1$C...$_3$C	$a_3=-0.063\pm0.003$	
x_4	C=C–$_1$C...$_4$C	$a_4=-0.033\pm0.004$	
x_5	C=C–$_1$C...$_5$C	$a_5=-0.020\pm0.006$	
x_6	C=C–$_1$C...$_6$C	$a_6=-0.013\pm0.009$	
x_7	C=C–$_1$C...$_7$C	$a_7=-0.008\pm0.010$	0.109
x_8		$a_8=0.374\pm0.012$	0.066
x_9		$a_9=0.245\pm0.012$	0.043
x_{10}		$a_{10}=-0.205\pm0.017$	0.029
x_{11}		$a_{11}=0.159\pm0.031$	0.027
x_{12}		$a_{12}=0.022\pm0.004$	0.024
x_{13}		$a_{13}=0.016\pm0.003$	0.021

Table 4. The designation of compounds is that of Table 1.

Table 4

Examples for Defining the Regressors

Compounds	Regressors
	0. 1. 2. 3. 4. 5. 6. 7. 8. 9.10.11.12.13.
1. 0,0,0,0	1; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0
12. 7,0,0,0	1; 1; 1; 1; 1; 1; 1; 1; 0; 0; 0; 0; 0; 0
30. 1,t4,0,0	1; 2; 3; 0; 0; 0; 0; 0; 0; 1; 0; 0; 3; 3
107. t4,t4,t4,0	1; 3; 9; 0; 0; 0; 0; 0; 1; 2; 1; 0;12; 9
121. 3,2,2,2	1; 4; 4; 1. 0; 0; 0; 0; 2; 4; 4; 1; 8; 0

A statistical processing of data has been carried out within the frames of Eq. 7, by using the method of least squares described in [17]. The respective coefficients of Eq.7 and their errors are given in Table 3. In the last column of Table 3 there are standard errors of calculation if Eq.7 is not used to its full capacity. Taking into account the regressors x_0-x_7, i.e. only the numbers of carbon atoms in different positions, we obtain the accuracy s=0.109 eV. This is rather a low accuracy but still better than that of the universal method of paper [14]. A successive inclusion of the regressors x_8, x_9 and x_{10} makes the results much better. The standard error decreases to 0.066, 0.043 and 0.029 eV, respectively. When taking into account the whole set of regressors, we obtain the result of s=0.021 eV.

The statistical parameters of describing the IP by Eq. 7 are the following:

n (number of compounds) = 121;

M (the number of IP values) = 163;

s (the standard error) = 0.021 eV;

$s\% = s\ 100/(I_{max}-I_{min})=0.845$, where I_{max} and I_{min} are the maximum and minimum value of IP in Table 1;

R (multiple correlation coefficient) = 0.9996.

Eq. 7 describes rather accurately all the known IPs of

alkenes. Those compounds for which the difference between the calculated and the experimental IP value (ΔI) are of the order of 0.04–0.06 eV, are given in Table 5. The majority of those compounds (21, 23, 106, 107, 114) contains large tret-buthyl or neo-amyl substituents.

Table 5

The Differences $\Delta I = I_{exp} - I_{calc}$ between the Experimental and the Calculated IPs According to Eqs. 7 and 1 .

No. of compound (according to Table 1)	2	6	21	23	106	107	114
Eq. 7	+0.041	-0.045	-0.046	+0.047	+0.061	-0.054	+0.052
Eq. 1			-0.060		+0.056	-0.039	

In order to obtain an experimental accuracy in Eq. 7 we need 6 parameters, which characterize interactions between substituents and chains (x_8–x_{13}). Since the influence of the major part of these parameters on the accuracy of description is small (see the values of s in Table 3), we can consider as necessary only two (x_8 and x_9).

In this case we obtain

$$I = (10.461\pm0.011)x_0-(0.740\pm0.009)x_1-(0.058\pm0.003)x_2-$$
$$-(0.068\pm0.005)x_3-(0.038\pm0.008)x_4-(0.020\pm0.012)x_5-$$
$$-(0.011\pm0.018)x_6-(0.015\pm0.020)x_7+(0.202\pm0.009)x_8+$$
$$+(0.105\pm0.007)x_9, \qquad (7A)$$

n=121; M=163; s=0.043; s%=1.74; R=0.9983.

An essential role in the so-called effect of saturation belongs to gem-, cis- and trans-interactions, described by the regressors x_8 and x_9. Cis- and trans-interactions cannot be distinguished according to their value and they probably

take place through bands. The influence between alkyl groups in gem-positions is considerably greater. In this case, interactions between pseudo-π-orbitals of alkyl groups through spaces are possible.

A statistical processing of data has been carried out by using the computer EC-1022 of the Institute of Astrophysics and Atmospheric Physics of Estonian Academy of Sciences. A code of linear regression analysis from paper [19] has been used.

We are indebted to Jan Pelt for kindly providing us with translated code.

References

1. K. Watanabe, T. Nakayama, and J. Mottl , J. Quant. Spectrosc. Radiat. Transfer, 2, 369 (1962).
2. S. Rang, E. Märtinson, and M. Müürisepp, Eesti NSV Tead. Akad. Toimetised, Keem.Geol. 23, 352 (1974) (in Russian).
3. S. Rang, P. Põldoja, and A. Talvari, Eesti NSV Tead. Akad. Toimetised, Keem. Geol., 23, 354 (1974)(in Russian).
4. W.C. Price, R. Bralsford, and P.V. Harris, Spectr. Acta, 14, 45 (1959).
5. P. Masclet, D. Grosjean, and G. Mouvier, J. Electron Spectrosc. Relat. Phenom., 2, 225 (1973).
6. D.C. Frost,and J.S. Sandhu, Indian J. Chem., 9, 1105 (1971).
7. K.V. Wood and J.W. Taylor, Int. J. Mass Spectrom. Ion. Phys., 30, 307 (1979).
8. P. Bischof and E. Heilbronner, Helv. Chim. Acta, 53, 1677 (1970).
9. P. Põldoja, Eesti NSV Tead. Akad. Toimetised, Füüs. Mat. 25, 50 (1976) (in Russian).
10. F.I. Vilesov, Uspekhi Fotoniki, 1, 5 (1969) (in Russian).
11. R.D. Levin and S.G. Lias, Ionization Potential and Appearance Potential Measurements 1971-1981. Natl. Stand. Ref. Data Ser., 71 (1982).
12. P.A. Clark, Theoret. Chim. Acta, 28, 75 (1972).

13. M. Beez, G. Bieri, H. Bock, and E. Heilbronner, Helv. Chim. Acta, 56, 1028 (1973).
14. I.A. Koppel, U.H. Mölder, and R.I. Pikver, This journal, 18, 380 (1981).
15. I.A. Koppel, U.H. Mölder, and R.I. Pikver, This journal, 21, 222 (1984).
16. W.C. Herndon, J. Am. Chem. Soc., 98, 887 (1976).
17. P.Põldoja and T. Viik, Eesti NSV Tead. Akad. Toimetised. Füüs. Mat. 35 (1986).
18. P. Põldoja,and T. Viik, Eesti NSV Tead. Akad. Toimetised. Füüs. Mat., 35 (1986).
19. W.M. Gentleman, Appl. Statistics, 23, 448 (1974).

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ON FINE STRUCTURE OF n, π^* - ABSORPTION BAND OF (9, 10)- ANTHRAQUINONE

V.Ya. Fain, L.Ya. Kliot, Yu.V. Ivanov, T.M. Skotnikova, and B.E. Zaitsev
Research Institute of Organic Semiproducts and Dyes, Moscow

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Computed data on the fine structure of the n, π^* absorption band have been obtained via separation of the 9,10-anthraquinone absorption spectrum into vibrational contributions.

Quantitative regularities expressing the solvent effect on the π, π^* position as well as those concerning the main components of the n, π^*- band vibrational structure have been found.

The 9,10- anthraquinone derivatives have great practical value as dyes, pigments, luminescent solids, analytical reagents, biologically active compounds, medicaments and the catalysts of oxidation - reduction processes[1]. This has led to the intensive studies of the properties of these compounds, their electronic absorption spectra included.

Although the absorption spectra of the unsubstituted 9,10- anthraquinone have been described in approximately 200 literary sources, the weak long-wave n, π^* band causing a pale yellow color has been studied rather superficially. It appears in concentrated solutions only ($\sim 5 \cdot 10^{-3}$ g-mol/l) as a result of the prohibited $I_A - I_U$ transition. At low

concentrations it can hardly ever be observed, so the phenomenen has not been studied in several papers[2].

The n, π^*- band is broader than the other 9,10- anthraquinone absorption bands and has a well developed vibrational fine structure, which is especially clearly expressed in the vapor state as here the distance between the absorption peaks is ≈1400 cm^{-1} . The latter is characteristic of the carbonylic group vibration in the excited state[3]. In solutions the fine structure of the n, π^*- band depends on the solvent nature. In non-polar solvents it is revealed via the peaks and relatively clear transmissions between them. In polar solvents the fine structure is not clearly expressed (shapeless).

The transition of the solution to the solid, glass-like state at low temperatures favors the emergence of the fine band structure[2]. In the n, π^*- absorption spectra of the 9,10- anthraquinone frozen solutions, the variation of frequences between the components of the fine structure is 1660 cm^{-1} on the average thus corresponding to the CO-group stretching vibration frequency in the ground electronic state[3].

Different authors have given 1 to 6 components[2] in the n, π^*- absorption spectra of the 9,10- anthraquinone solutions. Difficulties in the determination of the bands' position, dependence of these results on the purity of the compound and solvents and on the solution concentration yielded different data in one and the same solvent. Therefore we considered it necessary to conduct some measurements once again.

9,10- anthraquinone and the solvents were purified according to the known methods. The absorption spectra were taken on a spectrophotometer Specord UV Vis, while the n, π^* absorption spectra were registered at the concentrations near to saturation. In order to better determine the position of the components of the n, π^*-band fine structure from the total absorption of the area (see, e.g. curve 1, Fig. 1), the π, π^* absorption (curve 2) was computed. Curve 3 obtained was decomposed by means of a computer Hulett-Packard 9100 B and DASQ - 2 STM into separate gaussian components[4]. The num-

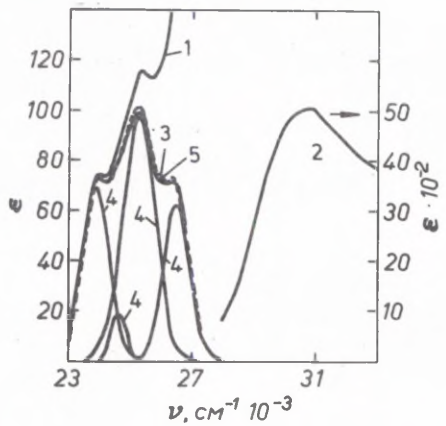

Fig.1. n, π^* absorption spectrum of 9,10- anthraquinone in toluene and the results of its decomposition into individual components (see explanations in the texts).

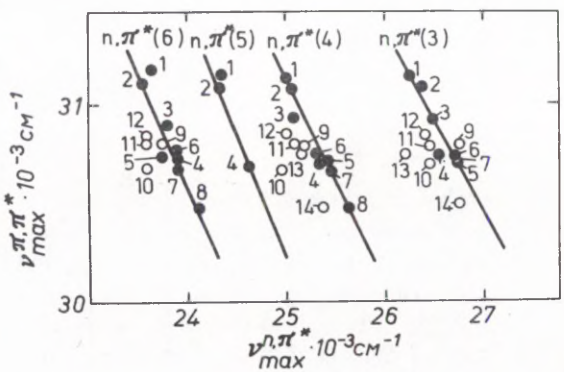

Fig. 2. Proportional susceptibility of the fine structure components of the n,π^* band of 9,10- anthraquinone and π, π^* band (solvents are given in Table).

ber of the components and their characteristics were determined by the methods of mathematical statistics as follows: first, approximately, according to the spectrum visualized on the screen of a TV-monitor; then the functional consisting of the sum of the square roots of spectrum deviations' from its approximated form expressed by the sum of gaussian 5 was made up. Finally, via the combination of coordinate and gradient methods as well as the corresponding Newton[4] approximations was found the (perhaps local) minimum of the function. The spectrum and its model were visualized once again, in the point of the greatest deviation another gaussian was added. If the latter operation gave a remarkable statistical improvement of the model dispersion, the cycle of calculations was repeated until the dispersion was stabilized.

The accuracy of the results depends on how exactly the n, π^* absorption curve is recorded. In case of 9,10-anthraquinone the curve is rather small, as, on the one hand the n, π^* - band is not intensive enough, and on the other hand, because of the limited solubility in organic solvents, which does not allow to increase the concentration of solutions. Nevertheless, decomposition enables one to get objective data which is reproducible in case of repeated runs. It is not usually possible in case of the ordinary visual determination of the bond positions at the absorption curves. One should differentiate between the aprotic and proton-donor solvents when discussing the effect of solvents' nature on the n, π^* absorption spectrum. The interaction with the former solvent type is of purely non-specific, mostly of the dipole-dipole character, while the latter form intermolecular hydrogen bonds with hydrogen atoms of the 9,10-anthraquinone carbonyl groups.

In aprotic solvents the fine structure of the 9,10-anthraquinone n, π^* absorption band remarkably depends on their polarity. In non-polar hexane 7 components can be detected, 3 of them form distinct peaks (see Table). The number of the components drops to 3 with the increase of the solvent polarity. The peaks turn into the bends which in the more polar dimethylsulfoxide are diffused to such a degree that the po-

Table

Classification of Fine Structure Elements of 9,10- Anthraquinone

n, π^* Band

No	Solvent	ν_{max}^{π,π^*} $cm^{-1}.10^{-3}$	Components of n, π^* band, ν_{max} · cm^{-1}. 10^{-3}						
			1	2	3	4	5	6	7
1	Hexane	31.16	28.63*	(27.77)	26.26*	25.00*	(24.33)	(23.62)	(23.24)
2	Cyclohexane	31.08	28.66*	(27.76)	26.34*	25.00*	(24.29)	(23.54)	(24.04)
3	4-Chloro carbon	30.92	-	27.70*	26.45*	25.05*	-	(23.80)	(23.47)
4	Toluene	30.72	-	-	26.52*	25.30*	(24.63)	23.90*	-
5	Benzene	30.72	-	-	26.69*	(25.40)	-	(23.73)	-
6	Triethylphosphate	30.76	-	-	26.70*	25.30*	-	(23.89)	-
7	Dimethylphormamide	30.68	-	-	26.70*	25.40*	-	(23.90)	-
8	Dimethylsulfoxide	30.48	-	-	(26.40)	25.59*	-	(24.13)	-
9	Methanol	30.80	-	(27.40)	26.71*	(25.20)	-	(23.77)	-
10	Ethanol	30.68	-	-	26.47*	(24.95)	(24.29)	(23.59)	-
11	Buthanol	30.80	-	-	26.49*	25.09*	-	(23.60)	-
12	2-Propanol	30.84	-	(27.10)	26.47*	(25.00)	-	(23.57)	-
13	2-Methyl-2-Propanole	30.76	-	27.26*	(26.20)	(25.15)	-	-	-
14	Ethylene glycole	30.48	-	-	26.75*	(25.37)	-	-	-

* Note: the components appearing in the initial spectrum as the absorption peak are marked with an asterisk the components having weak intensity, whose position is determined with an error are given in parentheses.

sition of separate components cannot be determined exactly enough.

In proton-donor alcohols, the components of the n, π^* band fine structure reveal only in the form of the absorption bands. Usually it is possible to distinguish between 3-4 components but in a highly polar ethylene glycole only 2 components can be found. The position of the latter is determined with a greater deviation than usual.

The Table shows that components 1,5 and 7 are observed in non-polar or slightly polar solvents only, though the position of 5 and 7 cannot be determined exactly enough. The position of components 3 and 4 can be detected more precisely, thus, they should be taken as the basic components.

The classification of the fine structure components of the 9,10- anthraquinone n, π^* band agrees with the regularities characterizing solvent effect on the position of these components.

Fig. 2 illustrates the proportional susceptibility of the long-wave π, π^* band and the fine-structure components of the 9,10- anthraquinone n, π^* band to the aprotio solvents. This example of the proportional shift of two different bands of the same compound effected by the solvents is especially interesting, since it concerns the band shifts of opposite directions. The values obtained in proton-donor solvents do not usually obey these regularities. Thus the problem whether these deviations are connected with the different interaction mechanism of the 9,10- anthraquinone interaction with aprotic and proton-donor solvents or only with the decrease in the accuracy of determining the position of the n, π^* band components in alcohols, remains unsolved.

Calculations were carried out on a computer "Mir" at 0.35 risk level. The following equations characterizing the dependences given in Fig. 2, were obtained:

$$\nu^{n,\pi^*(3)}_{max} = (53.70 \pm 12.25) - (0.88 \pm 0.40)\, \nu^{\pi,\pi^*}_{max} \ cm^{-1} \cdot 10^{-3}$$

Solvent number N=7, correlation coefficient r=0.93; standard deviation SD= 73 cm^{-1},

$$\nu_{max}^{n,\pi^*(4)} = (54.06\pm7.53)-(0.94\pm0.24)\,\nu_{max}^{\pi,\pi^*} \text{ cm}^{-1}\cdot 10^{-3}$$

N = 8, r = 0.960, SD = 61 cm^{-1}

$$\nu_{max}^{n,\pi^*} = (48.30\pm7.67)-(0.79\pm0.25)\,\nu_{max}^{\pi,\pi^*} \text{ cm}^{-1}\cdot 10^{-3}$$

N = 8, r = 0.954, SD = 59 cm^{-1}

From the above-mentioned facts follows also the regularity of the 9,10- anthraquinone n, π^*- band components' proportional susceptibility to aprotic solvents:

$$\nu_{max}^{n,\pi^*(3)} = (3.3\pm10.5)+(0.92\pm0.42)\,\nu_{max}^{n,\pi^*(4)} \text{ cm}^{-1}\cdot 10^{-3}$$

N = 7, r = 0.93, SD = 73 cm^{-1}

$$\nu_{max}^{n,\pi^*(6)} = (3.3\pm9.0)+(0.81\pm0.36)\,\nu_{max}^{n\,\pi^*(4)} \text{ cm}^{-1}\cdot 10^{-3}$$

N = 7, r = 0.93, SD = 77 cm^{-1}

In[5,6] we have established the applicability of the Kamlet-Taft[7] solvatochromic equation in case of a quantitative characterization of the $\pi 1,\pi^*$ shifts of the 9,10-anthraquinone derivatives under the influence of solvents. This equation can also be used for an approximate quantitative characterization of solvent effect on the unsubstituted 9,10-anthraquinone n, π^*- band components' frequency.

The following equations were obtained for the whole set of solvents (the proton-donor ones included):

$$\nu_{max}^{n,\pi^*(3)} = (0.57\pm0.22)(\pi^* - 0.086\,\delta) - (0.07\pm0.14)\alpha + \\ + (26.32\pm0.11) \text{ cm}^{-1}\cdot 10^{-3}$$

N = 13 (without dimethylsulfoxide), R = 0.88, SD=90 cm^{-1}

$$\nu_{max}^{n,\pi^*(4)} = (0.56\pm0.19)(\pi^* - 0.086\,\delta) - (0.21\pm0.14)\alpha + (24.99\pm0.11)\ cm^{-1}\cdot 10^{-3}$$

$N = 14,\quad R = 0.90,\quad SD = 100\ cm^{-1}$

where π^* denotes the solvatochromic parameter of nonspecific solvation (its values are known[7] for 124 solvents); $0.086\,\delta$ is the error coefficient taking into consideration the contribution of the solvents' polarizability, its application is recommended in[7] for the compounds with negative solvatochromy α signifies the solvatochromic parameter characterizing the proton-donor solvents' ability to form the intermolecular hydrogen bonds with proton-acceptor dissolved compounds[7].

Despite negligible standard deviation values, the correlation coefficients are small because of slight shifts of the n, π^* band components as well as a relatively great error of their determination.

The plus sign of coefficients in case of parameter $(\pi^* - 0.086\,\delta)$ refers to the hypochromic shift of the n, π^*-band, while the solvents' polarity increases. The minus sign of coefficients in case of parameter α evidences about its batochromic shift under the influence of intermolecular hydrogen bond. Coefficient value in case of the solvatochromic parameter is small, though for the n, $\pi^*(3)$ component, the value is statistically negligible. Consequently, the intermolecular hydrogen bond contribution into the 9,10-anthraquinone n, π - bond shifts under the solvent effect is insignificant.

According to Rodionov et al.[8], values $\Delta\nu = \nu_{max}^{gas} - \nu_{max}^{solvent}$ measured for the 9,10-anthraquinone long-wave π,π^* band in 5 different solvents represent linear medium function $f(\varepsilon, n^2)$, where ε is the dielectric constant, n is the solvent breaking indicator. These quantitative characteristics which do not take into account the intermolecular hydrogen bond effect are not presented.

We have found that the aprotic solvents' effect on the position of this band can be approximately described by means of the Kamlet-Taft equation:

$$\nu_{max}^{\pi,\pi^*} = (31.12 \pm 0.08) - (0.56 \pm 0.14)\pi^* \text{ cm}^{-1} \cdot 10^{-3}$$

$$N = 13, \quad r = 0.934, \quad SD = 72 \text{ cm}^{-1}$$

For the values measured in 19 different solvents:

$$\nu_{max}^{\pi,\pi^*} = (31.12 \pm 0.08) - (0.56 \pm 0.13)\pi^* - (0.094 \pm 0.092)\alpha \text{cm}^{-1} \cdot 10^{-3}$$

$$R = 0.922, \quad SD = 73 \text{ cm}^{-1}$$

In case of both solvatochromic parameters the minus sign of coefficients means that the specific as well as the non-specific interactions of 9,10- anthraquinone with solvents favors the batochromic shift of the long - wave π,π^* band. It proceeds from their coefficient values that non-specific interactions mostly, make their contribution into the above-mentioned shift, the contribution of intermolecular hydrogen bond being rather insignificant ($\approx$ 6 times smaller).

The equations presented enable us to calculate the position of the 9,10- anthraquinone long-wave π,π^* - and n, π^* absorption bands in a large number of solvents, whose solvatochromic parameters are known.

References

1. M.V. Gorelik, Chemistry of Anthraquinones and Their Derivatives, (in Russ.), Khimiya, Moscow, 1983.
2. V.Ya. Fain, Tables of Electronic Spectra of Anthraquinone and Its Derivatives, (in Russ.), Khimiya, Leningrad, 1970.
3. N.A. Borisevich, Excited States of Compound Molecules in Gas Phase, (in Russ.), Nauka i Tekhnika, Minsk, 1967.

4. B.P. Demidovich and I.A. Maron, Fundamentals of Applied Mathematics (in Russ.), Nauka, Moscow, 1970
5. V.Ya. Fain, L.Ya. Kliot, Yu.V. Ivanov, T.P. Kosacheva, and B.E. Zaitsev, Anilinokrasochn. promyshl., Vol. 5, 8 (1983).
6. V.Ya. Fain, L.Ya. Kliot, Yu.V. Ivanov, and B.E. Zaitsev, Organic Reactivity, 20, 467 (1983).
7. M.J. Kamlet, J.L.M. Abboud, and R.W. Taft, Progr. Phys. Org.Chem., 13, 485 (1981).
8. G.N. Rodionova, N.A. Partalla, and A.N. Rodionov, ZhFKh, 55, No 11, 2858 (1981).

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SOLVENT EFFECT ON POSITION OF $\pi 1$, π^* - ABSORPTION BANDS OF MONO(ALKYL, PHENYL) AMINOANTHRAQUINONES

B.Ya. Fain, L.Ya. Kliot, and B. E. Zaitsev
Research Institute of Organic Semiproducts and Dyes,
Moscow

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The Kamlet - Taft and Koppel - Palm equations have been applied in order to characterize quantitatively the solvent effect on the position of long wave $\pi 1$, π^* absorption bands of 1- and 2- mono(alkyl, phenyl) aminoanthraquinones. The contribution of different interaction types of these compounds with solvents has been estimated. The effects of substituent position in the anthraquinone nucleus as well as the alkylation and phenylation of the aminogroup were observed.

(Alkyl, aryl)amino-9,10- anthraquinones have great practical value as synthetic dyes, pigments and luminescent solids. Recently they have been used in a number of new fields of technology, e.g. in color photography and television, in the sphere of laser technology, in electro-optical equipment, etc.[1] For that reason the color intensity of this compound group has been studied throughout several decades (see, e.g. the review in[2]).

It has been established[3] that the solvent effect on the position of the long-wave $\pi 1$, π^* bands of some anthraquinone monosubstituents, determining the color of these com-

pounds can be quantitatively characterized by the multiparameter Kamlet - Taft and Koppel - Palm correlation equations based on the linear correspondence of solvation energy.

The Kamplet - Taft and Koppel - Palm equations can be applied in order to characterize the influence of the solvents on the parameters of various physico-chemical properties and on the reactivity of the dissolved compounds (see e.g.[4-6]). Evidently, studying the dependence on the solvent nature any of these parameters, the ν_{max} of the longwave absorption band included, gives valuable information about the interaction nature of the observed compounds with solvents.

The present paper deals with the influence of mono(alkyl, phenyl) aminoanthraquinones' chemical structure on their interaction with solvents.

The Kamlet - Taft[4] equation has been used for all compounds in such neutral solvents which cannot form intermolecular hydrogen bonds (IHB).

$$\nu_{max} = \nu_o + s\,\pi^* \qquad (1)$$

where ν_o denotes the position of the $\pi 1$, π^* absorption band in the standard solvent (cyclohexane), π^* is the solvatochromic parameter characterizing the non-specific solvation by the solvent and depends on its dipole moment value; s denotes the solvatochromic coefficient showing the compound's sensitivity to the non-specific solvation.

The characteristics of the obtained equations are given in Table 1.

According to the comparison of the values of solvatochromic coefficients, the 2-substituted isomers are more susceptible to the non-specific solvation than the 1-isomers. Substitution of the hydrogen atoms for the methyl residues in the 2-aminogroup leads to the decrease in the susceptibility: in case of one atom 2.78:1.96 = 1.4 times, and in case of two atoms 2.78:1.67 = 1.6 times. Similar substitution in 1-aminogroup causes the increase of susceptibility to the nonspecific solvation 0.86:0.66 = 1.3 and 1.01:0.66 = 1.5 times respectively. The substitution of hydrogen atom for the phenyl group is accompanied by the decrease of susceptibility

Table 1

Characteristics of Kamlet - Taft Solvatochromic Equations (1) in Neutral Solvents.

Equation	Anthraquinone substitute	$-10^{-3}\cdot\nu_o$ cm^{-1}	$-10^{-3}\cdot s$	Solvent number N	Correlation coefficient r	Standard deviation, cm^{-1} SD
1-1	1-NH_2 -	21.96±0.08	0.66±0.13	12	0.963	70
1-2	1-$NHCH_3$-	20.34±0.06	0.86±0.09	12	0.990	40
1-3	1-NHC_6H_5-	20.21±0.07	0.55±0.13	5	0.991	20
1-4	1-$N(CH_3)_2$-	20.44±0.08	1.01±0.11	11	0.989	50
1-5	1-NC_5H_{10}-	19.84±0.08	0.77±0.12	11	0.977	60
1-6	2-NH_2-	26.16±0.36	2.78±0.60	11	0.961	270
1-7	2-NHC_6H_5-	23.38±0.13	1.63±0.29	6	0.992	80
1-8	2-$N(CH_3)_2$-	22.62±0.09	1.67±0.14	9	0.995	50
1-9	2-NC_5H_{10}	22.85±0.07	2.23±0.23	10	0.991	90
1-10	2-$NHCH_3$-	23.75±0.13	1.96±0.25	5	0.998	50

(2.78:1.63 = 1.7 times at the 2-derivative and 0.66:0.55=1.2 times at the 1-derivative).

The general solvatochromic Kamlet - Taft[4] equation can be applied for the whole set of solvents:

$$\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta \qquad (2)$$

where solvatochromic parameter α characterizes the ability of proton-donor solvent to form the IHB with the proton-acceptor dissolved compound, and β shows the ability of proton-acceptor solvent to form the IHB with the proton-donor dissolved compound; solvatochromic coefficients a and b denote the compound's susceptibility to the corresponding interactions with solvents.

The characteristics of eq. (2) are given in Table 2.

Term $b\beta$ is absent in eqs. (2-4), (2-5), (2-8) and (2-9) for the compounds which do not contain an active hydrogen atom able to form the IHB with proton-acceptor solvents.This term turned out to be statistically negligible also in eq. (2-2). Consequently, the hydrogen atom of the 1-methylamino group related to the intramolecular hydrogen bond does not participate in the IHB (intermolecular hydrogen bond) formation. In eqs. (2-3) term $b\beta$ is statistically significant, though numerically rather small. It can be better seen in eqs. (2-3-1), obtained for aprotic solvents. This equation has a considerably greater correlation coefficient. It follows from this fact that the hydrogen atom of 1-aminogroup is only partly bound to the intermolecular hydrogen bond and it also to a certain extent takes part in the IHB formation with proton-acceptor solvents.

In case of all compounds, their susceptibility to the non-specific solvation is remarkably higher than to the interaction with proton-donor solvents. Alkylation of 1-aminoanthraquinone brings about the growth of its susceptibility to the proton-donor solvents 1.6 - 1.8 times, regardless of the existence of the intermolecular hydrogen bond. At the same time, the phenylation does not practically increase this type of susceptibility.

Table 2

Characteristics of Kamlet - Taft General Solvatochromic Equations (2)

Equation	Anthraquinone substitute	$10^{-3} \cdot \nu_0$, cm^{-1}	$-10^{-3} \cdot s$	$-10^{-3} \cdot a$	$-10^{-3} \cdot b$	N	Multiple correlation coefficient R	SD, cm^{-1}
2-1	1-NH_2-	21.96±0.06	0.64±0.09	0.17±0.09	0.68±0.10	22	220.989	60
2-2	1-$NHCH_3$-	20.33±0.07	0.84±0.11	0.30±0.08	-	17	0.978	60
2-3	1-NHC_6H_5-	20.23±0.08	0.54±0.15	0.19±0.11	-(0.15±0.13)	14	0.937	50
2-3-1	- " -	20.25±0.08	0.60±0.15	-	-(0.22±0.13)	10	0.967	50
2-4	1-$N(CH_3)_2$-	20.42±0.10	0.98±0.14	0.30±0.09	-	17	0.972	60
2-5	1-NC_5H_{10}-	19.87±0.10	0.83±0.15	0.27±0.14	-	15	0.964	80
2-6	2-NH_2-	26.10±0.30	2.71±0.47	0.79±0.34	2.39±0.36	22	0.985	260
2-7	2-NHC_6H_5-	23.36±0.16	1.47±0.32	0.49±0.28	1.22±0.30	16	0.990	130
2-8	2-$N(CH_3)_2$-	22.58±0.21	1.60±0.32	0.68±0.20	-	13	0.970	130
2-9	2-NC_5H_{10}-	22.85±0.07	2.23±0.07	0.80±0.05	-	16	0.968	130
2-10	2-$NHCH_3$-	23.68±0.22	1.68±0.39	0.64±0.31	1.24±0.34	15	0.989	150

The 2-substituted ones tend to be more susceptible to the proton-donor solvents than the 1-substituted ones. However, 2-aminoanthraquinone is 0.79:0.17 = 4.7 times more susceptible than its isomer, while that of 2-dimethylaminoanthraquinone is only 0.68:0.30 = 2.3 times greater.

The solvent effect on the position of the $\pi 1$, π^{*} - bands of studied compounds can be quantitatively described also by means of the Koppel - Palm[5] equation (3), although the statistical characteristics are somewhat less favorable (Table 3):

$$\nu_{max} = \nu_{o} + y\frac{\varepsilon-1}{2\varepsilon+1} + p\frac{n^2-1}{n^2+2} + eE + bB \quad , \qquad (3)$$

where ν_o is ν_{max} in vaporous phase, ε is the dielectric constant , n is the refraction indicator. E and B are the parameters of general acidity and basicity of the solvents; y,p,e,b are the coefficients dependent on the compound structure characterizing its susceptibility to the effect of the corresponding solvent properties.

According to the Koppel - Palm[5] method, the contributions of individual types of interaction with solvents are determined by the decrease in the R value when separate terms are excluded in turn from equation (3). The data presented in Table 4 show that in case of all mono (alkyl,phenyl) aminoanthraquinones nonspecific interactions with solvents play the most important role. In all cases, the effect of the solvents' general acidity is comparatively small.

If equations (2) enable to evaluate the contribution of general nonspecific interactions of the dissolved compound with solvents in comparison with specific interactions, it is possible by means of eq. (3) to differentiate between the polarity and polarizability effects of solvents. These effects turned out to be different in case of the compounds studied. Thus, the polarity contribution in case of the 2-amino, 2-anilino-, 1- and 2- dimethylaminoderivatives exceeds that described by the function of the refraction indicator. In case of the 1-methylamino, 1-anilino-, 1- and 2-piperidinoderivatives it is vice versa, while for 1-amino-

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Table 3

Characteristics of Koppel - Palm Solvatochromic Equations (3)

Equation	Anthraquinone substituents	$10^{-3}\nu_o$ cm^{-1}	$-10^{-3}y$	$-10^{-3}p$	-e	-b	N	R	SD cm^{-1}
3-1	1-NH_2-	23.23±0.49	1.48±0.60	3.98±1.71	22±10	1.9±0.6	24	0.986	80
3-2	1-$NHCH_3$-	21.97±0.65	1.78±0.75	5.54±2.38	27±20	-	15	0.949	120
3-3	1-NHC_6H_5-	21.30±0.39	0.83±0.32	3.98±1.36	9.8±8.8	-	13	0.948	50
3-4	1-$N(CH_3)_2$-	21.43±0.51	1.88±0.58	3.24±1.69	-	0.65±0.53	15	0.947	100
3-5	1-NC_5H_{10}-	21.38±0.65	1.61±0.68	5.21±2.27	23±21	-	14	0.951	110
3-6	2-NH_2-	29.63±2.38	5.77±2.57	10.63±8.22	83±64	6.1±2.4	21	0.974	370
3-7	2-NHC_6H_5-	25.34±1.48	3.48±1.84	5.81±5.34	58±44	2.5±1.3	15	0.969	250
3-8	2-$N(CH_3)_2$-	25.36±1.36	3.72±1.11	9.35±4.82	33±29	-	12	0.949	190
3-9	2-NC_5H_{10}-	25.89±1.41	4.21±1.57	10.67±4.73	47±40	-	15	0.943	250
3-10	2-$NHCH_3$-	25.48±1.74	4.84±2.04	8.38±6.02	49±43	2.1±1.7	14	0.972	250

and 2-methylamino substituents these contributions are similar to those given above.

It follows from eqs. (2-1) and (2-4) that the ν_{max} susceptibility of 1-dimethylaminoanthraquinone to the nonspecific interactions with solvents increase 0.98:0.64=1.5 times, as compared with the 1-aminosubstituted ones. Equations (3-1) and (3-4) show more precisely that this is mostly connected with the greater susceptibility to the polarity of the solvents, which increases 1.88:1.48 =1.3 times, while the growth in the susceptibility to the solvents' polarizability is 1.61:1.48 =1.1 times, only. It can be seen from eqs. (2-1) and (2-5) that during the transition from 1-amino- to 1-piperidine substituent, the ν_{max} susceptibility to the nonspecific interactions with solvents increases 0.83:0.64= = 1.3 times. At the same time the susceptibility to the polarizability of the solvents increases 5.21:3.98 = 1.3 times, but the susceptbility to the solvents' polarity decreases 3.98:3.24 = 1.2 times.

Table 4.

Variation of Correlation Coefficient in Case of Exclusion of Separate Terms from Eq. (3) According to Koppel-Palm

Equation	Anthraquinone substituents	R 4 parameters are taken into account	R in case of parameter exclusion			
			E	B	f(ε)	f(n)
3-1	1-NH_2-	0.986	0.969	0.933	0.953	0.958
3-2	1-$NHCH_3$-	0.955	0.908	0.949	0.854	0.817
3-3	1-NHC_6H_5-	0.955	0.910	0.948	0.768	0.649
3-4	1-$N(CH_3)_2$-	0.948	0.947	0.930	0.770	0.886
3-5	1-NC_5H_{10}-	0.951	0.921	0.951	0.868	0.812
3-6	2-NH_2-	0.974	0.958	0.914	0.926	0.959
3-7	2-NHC_6H_5-	0.969	0.951	0.933	0.931	0.957
3-8	2-$N(CH_3)_2$-	0.949	0.921	0.949	0.705	0.860
3-9	2-NC_5H_{10}-	0.945	0.910	0.943	0.844	0.803
3-10	2-$NHCH_3$-	0.971	0.957	0.955	0.908	0.905

Table 5

Position of $\pi 1$, π^* - Bands of Mono(Alkyl, Phenyl)Aminoanthraquinones

Solvent	$10^{-3}\ \nu_{max}$, cm^{-1}							
	1-$NHCH_3$-	1-NHC_6H_5-	1-$N(CH_3)_2$-	1-NC_5H_{10}-	2-$NHCH_3$-	2-NHC_6H_5-	2-$N(CH_3)_2$-	2-NC_5H_{10}-
1	2	3	4	5	6	7	8	9
Hexane	20.41[8]	10.28	20.48	19.92	23.92	23.58[2]	22.78[2]	23.12
Cyclohexane	20.32	-	-	19.84	-	23.36	-	-
Carbon tetrachloride	20.12[2]	20.02	20.18[2]	19.52	23.20[2]	22.84	22.12[2]	22.03
Toluene	19.88	19.92	-	19.52	22.64	22.44	-	21.69
Benzene	19.80[2]	19.88	19.88	19.36	22.56	22.40	22.64	21.50
Chlorobenzene	19.69[9]	-	19.80	19.28	-	22.32[2]	-	21.23
Chlorophorm	19.76[2]	-	19.64	19.23[2]	22.32[2]	-	21.28	21.10[12]
Dichloro - methane	19.68[2]	19.80	19.68	-	22.48	-	21.28[2]	-
Dioxane	19.92	20.04	19.92	19.52	22.24	22.24	21.76	21.74
Ethyl acetate	-	20.08	19.88	-	-	22.08	-	-
Acetone	-	-	19.76	19.32	-	-	21.44	21.28
Triethyl-phosphate	-	20.00	-	-	21.60	21.44	21.50	-
Pyridine	19.65[10]	-	-	-	-	21.05[2]	-	-

Table 5 continued

1	2	3	4	5	6	7	8	9
Dimethyl-phormamide	19.53[8]	19.84	19.48	19.19	21.28	21.28	-	20.96
Dimethyl-sulfoxide	19.45	19.76	19.40	19.04	21.16	21.08	21.01	20.66
Methanol	19.61[2]	19.88	19.66	-	21.52	21.41[2]	21.19[2]	20.96
Ethanol	19.68	19.92	19.64[2]	-	21.24	21.20	21.23[2]	20.88
1-Propanol	19.60	-	19.72	19.20	-	-	-	20.88
2-Propanol	-	19.92	19.68	19.42[11]	21.24	21.04	21.20	21.37[11]
Butanol	19.72	19.92	19.68	19.24	21.20	-	21.10	-
1-Methyl-2-propanol	19.68	-	19.72	-	21.12	21.08	-	21.00
Phenylethanol	-	-	-	18.80	-	-	-	20.24

Equations (2) and (3) give approximate evaluation of the contributions of various mono(alkyl,phenyl)aminoanthraquinones' interactions. The minus at the coefficients in eqs. (1-3) refers to the fact that all those interactions lead to the bathocronic solvent shift of the $\pi 1$, π^* absorption band of the compounds studied. Both methods allow to calculate the ν_{max} values in a great number of solvents, the values of the corresponding parameters of which are known. Eqs.(1) and (2) guarantee better reliability than eq. (3).

Experimental

Compounds and solvents have been obtained and purified according to the known methods. The absorption spectra were taken on spectrophotometers SF-4 and Specord UV-Vis, literature data (see Table 5) were used. $\mathcal{E}$ and n were taken from[6], solvatochromic parameters π^*, α and β from[4], B and E from[7]. The calculations were carried out on a computer "Mir-1" with the 0.95 accuracy. The authors express their gratitude to Yu.V. Ivanova and T.M. Kosacheva who helped them to do the calculations.

References

1. M.V. Gorelik, The Chemistry of Anthraquinones and Their Derivatives, (in Russ.), Khimiya, Moscow, 1983.
2. V.Ya. Fain, "Tables of Electronic Spectra of Anthraquinone and Its Derivatives" (in Russ.), Khimiya, Leningrad, 1970.
3. V.Ya. Fain, L.Ya. Kliot, Yu.V. Ivanov, and B.E. Zaitsev, Organic Reactivity, 20, 467 (1983).
4. M.J. Kamlet, J.L. Abboud, and R.W. Taft, Progr.Phys.Org. Chem.,13, 485(1981).
5. I.A. Koppel and V.A. Palm In: "Advances in Linear Free Energy Relationship", Plenum Press, London-New York, 1972, P. 208.
6. R.G. Makitra and Ya.N. Pirig, Organic Reactivity, 16, 495(1979).
7. I.A. Koppel and A.I. Paju, Reakts. sposobn. organ. soedin., 11, 121, 139(1974).

8. G.N. Rodionova, I.V. Krutovskaya, A.N. Rodionov, Yu.G. Tuchin, and V.V. Karpov, ZhPS, 32, 623(1980).
9. Yu.G. Gerasimenko and N.T. Poteleschenko, ZhOrKh, 7,11, 2415 (1971).
10. H. Hemzavi and F. Janes, J.Soc. Dyers Colour, 85, No 9, 401(1969).
11. G.O. Phillips, A.K. Davies, J.F. Mc Kellar, and D.Price, J.Chem.Soc., Chem.Comm., 1097(1969).
12. B.E. Zaitsev, Doctor Thesis, (in Russ.), Moscow,NIOPIK, 1975.

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INTERACTION OF BUTYL BROMIDE WITH MAGNESIUM IN PRESENCE OF BUTYL ETHER. NOVEL DETAILS OF THE REACTION MECHANISM.

A. Tuulmets, M. Hörak, K. Sarv, and E. Aaresild
Dept. of Organic Chemistry, Tartu State University,
202400, Tartu, Est.SSR.

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The reaction of butyl bromide with magnesium in toluene with additions of butyl ether from 0.4 to 0.79 mole to a mole of the halide was investigated kinetically. The earlier found features of the reaction were observed also in this case. The catalyses by solvated Grignard reagent was confirmed. The reaction of Grignard reagent with free radicals is essential in the formation of by-products.

Recently we found[1] that the formation of Grignard reagent in toluene in the presence of small amounts of ethyl ether (less than one mole to a mole of the halide) proceeds by steps. After a rapid formation of monosolvated Grignard reagent a slow completion of the reaction occurs under the influence of solvated alkylmagnesium halide present.

To check up whether the observed reaction course is not a specific effect of ethyl ether, we decided to examine the process in the presence of butyl ether whose effective basicity towards organomagnesium compounds is expected to be lower than that of ethyl ether[2].

In this investigation the same reaction of n-butyl bromide with magnesium in toluene was chosen as a model process.

Butyl ether was added in amounts from 0.40 to 0.79 mole to a mole of the halide. The process was followed by taking aliquots (by titration of the Grignard reagent and magnesium halide formed). The products were determined by means of g.l.c. Some special experiments enabled to clarify the mechanisms of formation of by-products.

Experimental Section

Reagents and Solvents.

Toluene was treated with conc. sulfuric acid, washed, dried over heated calcium chloride and fractionated over sodium wire.

The ethers were shaked with potassium hydroxide, and distilled over sodium wire, n-butyl bromide and n-hexyl bromide were dried over heated calcium chloride and fractionated.

Magnesium metal was used in the form of granules from 1.0 to 1.6 mm in diameter.

Kinetic Measurements

The reaction flask (a 35 ml Erlenmeyer flask) was capped with a teflon stopper which was equipped with a silicon rubber disk. The flask was placed into a glass vessel whose temperature was kept at $30\pm0.1^{\circ}C$ by means of a thermostate U-10. The reaction mixture was stirred by means of a magnetic stirring bar.

Before the kinetic runs 7.00 g of magnesium (0.29 g-atom, total surface about 185 cm^2) was placed into the flask.Toluene and butyl ether (altogether 20 ml in each run) were introduced into the flask by calibrated pipets. When the system had reached a constant temperature ($30^{\circ}C$), 3.0 ml of butyl bromide was introduced through the silicon rubber disk by a hypodermic syringe (0.028 g-mole, about 10% of the initial quantity of magnesium, a complete reacting of the halide causes the diminishing of the magnesium surface about 7%).

During the reaction at appropriate times aliquots of 1.0 ml were withdrawn and analyzed acidimetrically for the content of basic magnesium. In the same aliquots the amount of halide was determined by the Volhard method.

The kinetic curves were produced by plotting the yield of Grignard reagent against time.

Analysis of Reaction Mixture by G.L.C.

Reaction mixture was removed by use of a hypodermic syringe, decomposed by 0.1 N solution of sulfuric acid and extracted with ether. Etherious solution was dried over anhydrous sodium sulfate.

The analysis was carried out on a chromatograph "Svet-152" with a flame-detector. Column (3m) was filled with Inerton AW-DMCS (0.125-0.16 mm) coated with 10% Carbowax 20 M, the carrier gas was nitrogen, column temperature 56°C.

The relative content of octane, decane, and dodecane was determined. The areas of peaks were normalized according to the number of carbon atoms in molecules of hydrocarbons.

RESULTS AND DISCUSSION

The kinetic curves of formation of butylmagnesium bromide are represented in Fig.1. Just as in the presence of ethyl ether, a relatively rapid formation of Grignard reagent be-

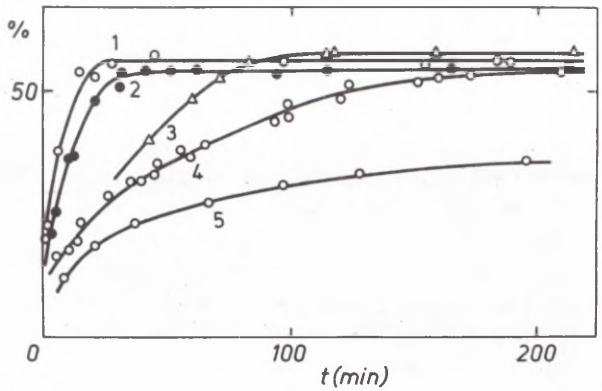

Fig.1.-Time-dependence of the yield of Grignard reagent at molar ratio of ether to butyl bromide:
1 - 0.79; 2 - 0.73; 3 - 0.62; 4 - 0.52; 5 - 0.40, the induction period is omitted.

gins after a certain induction period. However, the latter is considerably longer in this case.

The reaction has a complicated kinetics. A certain initial part of the process can be described by the first-order kinetics just as in the case of ethyl ether[1]. The rate constants were calculated by a differential method[3] from the slope of a plot of ln ($\Delta c/\Delta t$) vs. τ where c is the concentration of the Grignard reagent in an aliquot and τ is the time corresponding to the intermediate of the time-interval Δt. The constants obtained from such "linear" parts of differential curves are presented in Table 1.

Table 1.

The First-Order Rate Constants of Initial Stage of the Reaction

Relative content of ether	$k \cdot 10^3$, sec^{-1}	Relative content of ether	$k \cdot 10^3$, sec^{-1}
0.40	0.37 ± 0.05	0.73	1.85 ± 0.13
0.52	0.33 ± 0.02	0.73	2.33 ± 0.14
0.52	0.50 ± 0.08	0.79	7.01 ± 1.78
0.52	0.57 ± 0.07	0.79	8.11 ± 1.74
0.62	0.68 ± 0.02	0.79	8.24 ± 2.35

By analogy with the case of ethyl ether[1] we assume that in the region of small additions of butyl ether the values of first order rate constants also depend linearly on the ratio of ether to bromide (Fig. 2). However, a steep increase in reaction rate already begins at a molar ratio about 0.7 while in the case of ethyl ether it occurs only when ratio 1:1 is reached.

The features of the reaction in the presence of butyl ether are characterized by a relatively low yield of Grignard reagent (about 55%) and by considerable extent of Würtz reaction almost independent of the amount of the added ether in the range of examined molar ratios. It follows that the by-formation of magnesium bromide (so called Würtz reaction) is conjugated with Grignard reaction, or it proceeds competitively to the latter also being catalized by ether.

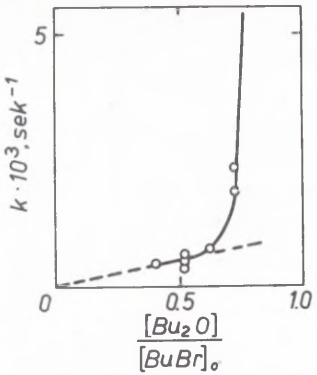

Fig.2. Dependence of first-order rate constant of initial stage of the reaction on molar ratio of ether and butyl bromide.

The above-mentioned conclusions enable us to explain why in our experiments with butyl ether we could not observe any slow zero-order step of the reaction (any separate reaction catalized by the solvated Grignard reagent[1]). By the time when ether is totally complexed with reaction products and further on only the zero-order reaction can proceed, butyl bromide is already completely spent. In order to verify this assumption, we carried out the following experiment. Into a reaction mixture where the reaction had completely come to an end, a new portion (also 3 ml) of butyl bromide was introduced and the reaction course was followed as usual. The same zero-order reaction as in the case of ethyl ether was observed (see also Fig. 3, rate constants are given in Table 2). Consequently, the reaction patterns detected by us earlier[1] prove to be general and the catalysis by the solvated Grignard reagent is confirmed.

Zero-order Rate Constants ($mole \cdot l^{-1} \cdot sec^{-1}$) for the Slow Step of Grignard Reagent Formation. Table 2.

Relative content of ether	$k_o \cdot 10^5$ from formation of	
	BuMgBr	$MgBr_2$
0.62	1.61 ± 0.10	3.44 ± 0.18
0.73	2.65 ± 0.22	4.39 ± 0.11
0.79	2.68 ± 0.19	4.33 ± 0.22

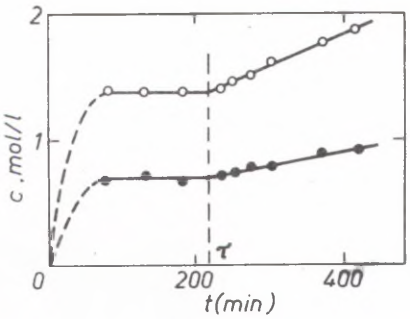

Fig. 3. Zero-order reaction after a new portion of butyl bromide was added at time τ. ● - concentration of butylmagnesium bromide, ○ - concentration of magnesium bromide

The conclusion that the formation of the Würtz-type products is conjugated with the Grignard reaction has aroused our interest in this side-reaction. The Würtz reaction products are usually considered as magnesium halide and a coupled hydrocarbon RR whose formation can be represented by the following stoecheometric equations

$$2\,RX + Mg \longrightarrow RR + MgX_2 \qquad (1)$$

$$RX + RMgX \longrightarrow RR + MgX_2 \qquad (2)$$

In order to check up the contribution of reaction (2) in our conditions, the following experiment was carried out: A sample (with ether content of 0.75 mole per mole of halide) that had reacted completely was separated from magnesium and allowed to react with a new portion (3 ml) of butyl bromide. The reaction was followed as in case of an ordinary kinetic experiment. Neither at 30°C nor at 80°C during three hours any changes in concentrations of Grignard reagent or magnesium bromide could be detected. A similar experiment was carried out while butyl ether was replaced by a more basic THF. After two hours at 30°C no changes were observed but at 80°C the concentration of magnesium bromide was increased by 15 per cent. This is in accordance with data[4] that reaction (2) is feasible at a raised temperature in the presence of strongly solvating bases. Thus, participation of reaction (2) in our

experiment can be excluded.

Concerning reaction (1), it is generally believed that coupled hydrocarbon results in the recombination of free radicals formed in a path from initial products to Grignard reagent. In order to examine this supposition, we carried out the following cross-experiment.

In conditions, close to the ordinary kinetic experiment, n-butyl bromide and n-hexyl bromide were made to react simultaneously, and consecutively - n-hexyl bromide after butyl bromide completely reacted. For the bases ethyl ether and THF were used. Relative amounts of formed octane, decane, and dodecane were determined by g.l.c. The results of the experiment are given in Table 3.

Table 3.

Relative Yields of Coupled Hydrocarbons in Cross-Experiment

No of run	Composition of the solvent, ml			Addition of halides m mole				Relative yield of		
	Et_2O	THF	Toluene	first		second		octane	decane	dodecane
1	2	-	18	BuBr	14.1			1.0	2.0	1.3
				HexBr	14.1	-				
2	2	-	18	BuBr	19.0	HexBr	21.3	1.0	0.33	1.7
3	10	-	10	BuBr	14.1	HexBr	14.1	1.0	0.24	1.1
4	-	1.2	18.8	BuBr	14.1					
				HexBr	14.1	-		1.0	1.4	0.42
5	-	1	19	BuBr	14.1	HexBr	14.1	1.0	0.26	0.45

If coupled hydrocarbons form only as a result of the recombination of alkyl radicals, then, assuming close reactivity of butyl and hexyl bromides and also of the corresponding alkyl radicals, one can expect approximately equal yields of octane, decane (the cross-product), and dodecane when the both halides will react simultaneously. Respectively, when the halides are added one after another, the cross-product can not appear.

In our experiment with simultaneous reaction of the halides, the yield of decane markedly exceeds those of other hydrocarbons (Table 3, runs 1 and 4) .This fact, and considerable formation of the cross-product in the consecutive reaction of halides (runs 2, 3, and 5) lead one to the

conclusion that a certain role in formation of coupled hydrocarbons (Würtz-type products) is engaged by a reaction of Grignard reagent with intermediate particles of the Grignard reaction, most probably with free radicals.

Then, for the simultaneous reaction, assuming close reactivities of butyl- and hexylmagnesium bromides and correspondingly that of butyl and hexyl radicals, one can expect a ratio of yields of coupled hydrocarbons close to 1:2:1. Such a ratio was actually obtained (runs 1, and 4). The appearance of the cross-product in consecutive reaction of halides was mentioned above. The other observed relations also agree with our conception about the course of this reaction. So, in run 2 the amount of ether was only sufficient for the consumption of butyl bromide in rapid reaction stage, while hexyl bromide reacted in slow stage where the contribution of the Würtz reaction is considerable[1]. These circumstances are well reflected in relative yields of products . In run 3, the amount of ether enabled the halides to react in equal conditions that caused a decrease in relative yields of dodecane and cross-product.

Although the formation of Würtz-type products in consequence of free radical recombination cannot be excluded, a considerable contribution of reactions of the Grignard reagent with free radicals should be taken into account subsequently. According to the conception of Palm and Hörak[5,6], these reactions may be as follows

$$RMgX + R^{\bullet} \longrightarrow RR + {}^{\bullet}MgX$$

$$RMgX + {}^{\bullet}MgR \longrightarrow RR + {}^{\bullet}MgX + Mg$$

$$RMgX + {}^{\bullet}MgX \longrightarrow {}^{\bullet}MgR + MgX_2$$

$$RMgX + X^{\bullet} \longrightarrow R^{\bullet} + MgX_2.$$

It is evident that none of these reactions leads to the interruption of the chain reaction. That is what the conjugation between the formation of the Grignard reagent and the Würtz type products consists in. The role of solvent in these reactions still needs some elucidation. Although the solvating solvent probably participates in both processes, a de-

crease in the amount of the base as well as in its solvating ability causes an increase in the contribution of the Würtz reaction.

References.

1. A. Tuulmets, M. Hörak, E. Pill, and A. Riikoja, Organic Reactivity, 22,No 1(77), 93 (1985)
2. A. Tuulmets, Organic Reactivity, 11,No 1(39), 81 (1974)
3. E.S. Rudakov, Akad.nauk SSSR, Kinetika i kataliz, 1, 177(1960)
4. L. Zakharkin, O. Okhlobystin, and K. Bilevich, Tetrahedron, 21, 881(1965).
5. V.A. Palm and M.P. Hörak, Dokl.An SSSR, 130, 1260(1960)
6. M. Hörak, V. Palm and U. Soogenbits, Organic Reactivity, 11,No 3(41),709 (1975)

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STRUCTURAL THEORY OF ELECTROLYTE SOLUTIONS. III ACTIVITY COEFFICIENTS OF 1:2 AND 2:1 ELECTROLYTES IN AQUEOUS SOLUTIONS.

M.M. Karelson and T. Sepp
Laboratory of Chemical Kinetics and Catalysis, Tartu State University, 202400 Tartu, Estonian S.S.R., U.S.S.R.

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Statistical verification of the structural theory of electrolyte solutions is proceeded on the basis of 1:2 and 2:1 electrolyte activity coefficients data at 25°C in aqueous solutions.

The structural dependence of the specific ion-solvent interaction parameter, V_s for electrolytes of different charge types has been discussed.

A simple structural theory of equilibrium electrolyte solutions was presented in the first article of this series[1]. This work deals with the application of this theory to the activity coefficients data of unsymmetrical 1:2 electrolytes in aqueous solutions. The concentration dependence of the activity coefficients of these electrolytes, $\gamma_\pm$ is represented by the following equation[1]:

$$\ln \gamma_\pm = a_t \sqrt[3]{c} + B_{ij} c \qquad (1)$$

The parameter

$$a_t = \frac{\alpha z_i z_j A_M}{\sqrt{\varepsilon RT}} , \qquad (2)$$

where A_M is the Madelung constant of the simplest lattice for the 1:2 and 2:1 electrolytes (presumably that of the CaF_2 type, $A_M = 2.520$[1,2]), z_i and z_j are the ionic charges of cations and anions, respectively, α - the energy scaling constant, ε - the macroscopic dielectric permittivity of solvent, R - the universal gas constant and T - absolute temperature, represents the multiplier in the purely electrostatic interionic interaction term according to the lattice theory of ionic solutions[3-6]. This term is the same for every electrolyte of a given type.

The parameter

$$B_{ij} = 2V_{s(ij)} \qquad (3)$$

is specific for any electrolyte and characterizes the intensity of its influence on the structure of the solvent (water). The positive values of structurization volume $V_{s(ij)}$ correspond to the structure-making, and negative values, respectively, to the structure-breaking of the solution in the vicinity of electrolyte ions.

The least-squares treatment of the activity coefficient logarithms was made in two ways.

First, the two-parameter equation (1) was used in form

$$\ln \gamma_{\pm} = \Delta \ln \gamma_{\pm} + a_t \sqrt[3]{c} + B_{ij} c \,, \qquad (4)$$

where a_t and B_{ij} are the parameters to be found. It is natural to use the intercept $\Delta \ln \gamma_{\pm}$, because almost all the published activity coefficients are standardized against the infinite dilution according to some function of square root of electrolyte concentration or ionic force. Therefore, the zero value ($\gamma_{\pm} = 1$), corresponding to Eq. (4), is shifted by a small quantity (0.1 - 0.3 units, see Table 1.)

The statistical fitness parameters given in Table 1, were excellent for practically every individual activity coefficients' set investigated (standard deviation $s < 0.05$ units, normalized standard error[1] $s_o < 0.02$ and correlation coefficient $r > 0.995$ for most cases). The data of cadmium halogenides are much worse described by Eq. (4) than these of other 2:1 electrolytes. However, a strong ion complexation is es-

tablished for these salts by several different experimental methods[7,8]. Therefore, it must cause a significant deviation of the experimental activity coefficients from the theoretical curve given by Eq. (4). For that reason the results of the statistical treatment of activity coefficients data of cadmium halogenides are not included in Table 1-2. For other 2:1 and 1:2 electrolytes, the a_t parameter is close to its theoretical value ($a_{t(theor)} = -1.4493$ in aqueous solutions at 25°C).

Correspondingly a secondary statistical treatment of data was carried out according to the equation:

$$\delta \ln \gamma_{\pm} = \Delta \ln \gamma'_{\pm} + B_{ij} c \qquad (5)$$

where the function to be correlated is

$$\delta \ln \gamma_{\pm} = \ln \gamma_{\pm} - a_{t(theor)} \sqrt[3]{c} \qquad (6)$$

i.e. the activity coefficient logarithm corrected by the theoretical electrostatistical term. Due to the above-mentioned different standardization of published activity coefficients, intercept $\Delta \ln \gamma'_{\pm}$ is used again. The results of the activity coefficients treatment according to Eq. (5) are given in Table 2, The validity of simple linear relationship (5) for some electrolytes is illustrated in Fig. 1. The contraction of the number of parameters to be found in treatment does not change noticeably the characteristics of the statistical fit (cf. Table 1. and 2.). Recalling the difference in the data sets for the same electrolyte, the fit of the theory almost in the limits of experimental error can be concluded. A number of 2:1 electrolytes have a very good solubility in water. Therefore their concentration in solutions can be very high, close to the concentration of water. Obviously the model about the specific solvent structure around the ions is not valid in such solutions where the number of ions is comparable with the number of water molecules. In case of several electrolytes, the deviations from Eq. (5) are observable at very high electrolytic concentrations in solutions. Therefore the statistical treatment was carried out in up to 2.0 - 4.0 m solutions to avoid these deviations. It must

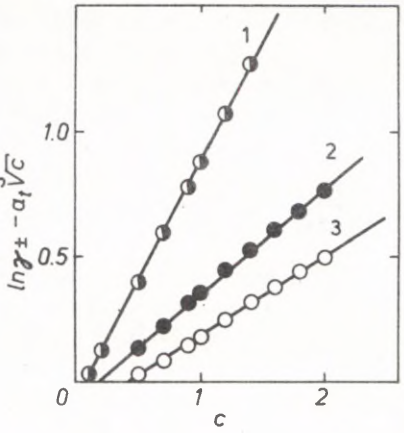

Fig. 1. The validity of Eq. (5) for some electrolytes in aqueous solutions (1-$MgCl_2$, 2-$Ca(NO_3)_2$, 3-Li_2SO_4)

be noted that up to this, some critical concentration, the parameters of Eq. (4) and (5) are constants independent of the number of points included in statistical treatment. The critical concentration usually corresponds to 4-8 molecules of water per 1 ion in solutions. This number is large enough to form a solvent-like structure in the vicinity of any individual ion in solution.

For the theoretical extension of the simple structural model of electrolyte solutions presented in this series of articles, the analysis of B_i-parameters should be of utmost interest.

To make these data comparable with those of 1:1 electrolytes, the concentration scales are to be unified. The concentration of anions is twice as high as in the 2:1 electrolytes in comparison with 1:1 electrolyte solutions of the same molar concentration, indeed. Therefore the corresponding V_s-parameters of 2:1 electrolytes obtained from the linear relationships on the molarity should be divided by two, and also the unified parameter

$$B_{ij(1:1)} = B_{ij}/2 \qquad (7)$$

Table 1

Results of Least-Squares Treatment of Activity Coefficients of 2:1 and 1:2 Electrolytes in Aqueous Solutions at 25°C According to Eq. (4).

No	Electrolyte	$\Delta \ln \gamma_{\pm}$	a_t	B_{1j}'	r^a	s^b	s_o^c	Reference
1	2	3	4	5	6	7	8	9
1.	$MgCl_2$	0.029±0.030	-1.645±0.054	1.124±0.022	0.999	0.010	0.011	10.
2.	$MgCl_2$	0.075±0.021	-1.600±0.037	1.101±0.015	0.999	0.008	0.007	11.
3.	$MgCl_2$	0.018±0.022	-1.617±0.038	1.098±0.016	0.999	0.008	0.008	12.
4.	$MgBr_2$	0.087±0.042	-1.777±0.077	1.454±0.033	0.999	0.014	0.011	10.
5.	$MgBr_2$	0.114±0.030	-1.677±0.054	1.376±0.023	0.999	0.010	0.008	11.
6.	MgI_2	0.276±0.081	-2.128±0.109	1.859±0.066	0.999	0.026	0.016	10.
7.	MgI_2	0.317±0.067	-2.135±0.127	1.901±0.062	0.999	0.019	0.015	11.
8.	MgI_2	0.285±0.067	-2.137±0.119	1.846±0.051	0.999	0.023	0.012	12.
9.	$Mg(ClO_4)_2$	0.239±0.086	-2.019±0.016	1.853±0.070	0.999	0.028	0.017	10.
10.	$Mg(ClO_4)_2$	0.192±0.059	-1.894±0.106	1.731±0.044	0.999	0.021	0.011	11.
11.	$Mg(ClO_4)_2$	0.194±0.062	-1.897±0.109	1.731±0.045	0.999	0.022	0.011	12.
12.	$Mg(NO_3)_2$	-0.084±0.010	-1.414±0.017	0.948±0.007	0.999	0.003	0.005	10.
13.	$Mg(NO_3)_2$	-0.111±0.006	-1.346±0.011	0.895±0.004	0.999	0.002	0.003	11.
14.	$(CH_3COO)_2Mg$	-0.120±0.009	-1.537±0.015	0.546±0.006	0.999	0.003	0.009	11.
15.	$(CH_3COO)_2Mg$	-0.178±0.014	-1.428±0.021	0.498±0.006	0.999	0.008	0.010	12.
16.	$CaCl_2$	0.037±0.005	-1.675±0.014	1.002±0.009	0.999	0.008	0.008	10.

Table 1 continued

1	2	3	4	5	6	7	8	9
17.	$CaCl_2$	0.025±0.008	-1.598±0.017	0.956±0.010	0.999	0.010	0.010	11.
18.	$CaCl_2$	-0.025±0.014	-1.541±0.024	0.934±0.010	0.999	0.005	0.007	12.
19.	$CaBr_2$	0.073±0.038	-1.750±0.069	1.247±0.030	0.999	0.013	0.013	10.
20.	$CaBr_2$	0.063±0.030	-1.723±0.053	1.219±0.022	0.995	0.011	0.010	11.
21.	CaI_2	0.178±0.072	-1.939±0.093	1.571±0.058	0.999	0.023	0.018	10.
22.	CaI_2	0.191±0.059	-1.959±0.106	1.568±0.045	0.999	0.020	0.014	11.
23.	CaI_2	0.177±0.057	-1.928±0.101	1.547±0.043	0.999	0.019	0.013	12.
24.	$Ca(ClO_4)_2$	0.129±0.064	-1.803±0.117	1.498±0.051	0.999	0.021	0.016	10.
25.	$Ca(ClO_4)_2$	0.109±0.048	-1.747±0.085	1.437±0.035	0.999	0.017	0.011	11.
26.	$Ca(NO_3)_2$	-0.122±0.008	-1.382±0.015	0.471±0.006	0.999	0.003	0.009	10.
27.	$Ca(NO_3)_2$	-0.025±0.039	-1.550±0.069	0.522±0.028	0.991	0.014	0.038	11.
28.	$Ca(NO_3)_2$	-0.137±0.008	-1.345±0.014	0.449±0.006	0.999	0.003	0.009	12.
29.	$SrCl_2$	-0.020±0.019	-1.552±0.033	0.872±0.014	0.999	0.006	0.012	10.
30.	$SrCl_2$	-0.040±0.004	-1.514±0.007	0.825±0.003	0.999	0.002	0.004	11.
31.	$SrCl_2$	-0.018±0.015	-1.553±0.027	0.868±0.011	0.999	0.006	0.009	12.
32.	$SrBr_2$	0.106±0.051	-1.817±0.094	1.184±0.041	0.998	0.017	0.022	10.
33.	$SrBr_2$	0.095±0.040	-1.784±0.070	1.149±0.030	0.999	0.014	0.015	11.
34.	SrI_2	0.240±0.090	-2.084±0.168	1.604±0.076	0.998	0.028	0.025	10.
35.	SrI_2	0.208±0.065	-1.994±0.117	1.512±0.050	0.998	0.022	0.017	11.
36.	SrI_2	0.219±0.024	-2.043±0.126	1.548±0.054	0.998	0.024	0.018	12.
37.	$Sr(ClO_4)_2$	0.056±0.032	-1.743±0.058	1.336±0.024	0.999	0.011	0.009	11.

Table 1 continued

1	2	3	4	5	6	7	8	9
38.	$Sr(NO_3)_2$	-0.110 ± 0.012	-1.399 ± 0.020	0.254 ± 0.007	0.999	0.005	0.008	10.
39.	$Sr(NO_3)_2$	-0.147 ± 0.009	-1.324 ± 0.017	0.224 ± 0.007	0.999	0.003	0.005	11.
40.	$Sr(NO_3)_2$	-0.187 ± 0.022	-1.257 ± 0.034	0.219 ± 0.010	0.998	0.012	0.016	12.
41.	$Sr(NO_3)_2$	-0.160 ± 0.032	-1.314 ± 0.055	0.244 ± 0.021	0.998	0.012	0.019	15.
42.	$BaCl_2$	-0.056 ± 0.011	-1.411 ± 0.021	0.639 ± 0.010	0.999	0.003	0.015	10.
43.	$BaCl_2$	0.042 ± 0.007	-1.717 ± 0.024	0.799 ± 0.020	0.999	0.015	0.010	13.
44.	$BaCl_2$	-0.009 ± 0.014	-1.609 ± 0.029	0.733 ± 0.015	0.998	0.011	0.018	11.
45.	$BaCl_2$	-0.089 ± 0.009	-1.403 ± 0.016	0.636 ± 0.007	0.999	0.003	0.011	12.
46.	$BaCl_2$	-0.150 ± 0.013	-1.361 ± 0.020	0.622 ± 0.007	0.999	0.002	0.007	14.
47.	$BaBr_2$	0.001 ± 0.023	-1.600 ± 0.042	0.936 ± 0.019	0.999	0.007	0.015	10.
48.	$BaBr_2$	-0.017 ± 0.018	-1.578 ± 0.033	0.924 ± 0.014	0.999	0.006	0.011	11.
49.	$BaBr_2$	-0.004 ± 0.018	-1.584 ± 0.033	0.918 ± 0.014	0.999	0.006	0.011	12.
50.	BaI_2	0.162 ± 0.078	-0.961 ± 0.145	1.512 ± 0.067	0.998	0.024	0.023	10.
51.	BaI_2	0.144 ± 0.061	-1.907 ± 0.091	1.451 ± 0.050	0.998	0.020	0.017	11.
52.	$Ba(ClO_4)_2$	-0.062 ± 0.013	-1.442 ± 0.024	0.921 ± 0.011	0.999	0.004	0.008	10.
53.	$Ba(ClO_4)_2$	-0.062 ± 0.014	-1.441 ± 0.025	0.919 ± 0.011	0.999	0.005	0.007	11.
54.	$Ba(NO_3)_2$	0.042 ± 0.027	-1.917 ± 0.070	0.103 ± 0.064	0.999	0.002	0.005	10.
55.	$(CH_3COO)_2Ba$	-0.377 ± 0.042	-0.949 ± 0.074	0.267 ± 0.031	0.986	0.015	0.048	11.
56.	$ZnCl_2$	-0.092 ± 0.057	-1.217 ± 0.090	0.261 ± 0.028	0.985	0.027	0.051	10.
57.	$ZnCl_2$	-0.126 ± 0.044	-1.013 ± 0.094	0.118 ± 0.051	0.987	0.046	0.042	11.
58.	$ZnCl_2$	-0.268 ± 0.016	-0.871 ± 0.028	0.105 ± 0.011	0.999	0.006	0.011	12.

Table 1 continued

1	2	3	4	5	6	7	8	9
59.	$ZnCl_2$	0.001±0.016	-1.480±0.053	0.386±0.043	0.997	0.033	0.019	13
60.	$ZnBr_2$	-0.369±0.102	-0.569±0.155	0.347±0.043	0.979	0.055	0.056	10.
61.	$ZnBr_2$	-0.348±0.058	-0.580±0.109	0.352±0.050	0.925	0.030	0.105	11.
62.	$ZnBr_2$	-0.555±0.069	-0.231±0.123	0.225±0.051	0.953	0.025	0.087	12.
63.	ZnI_2	-0.816±0.137	0.330±0.227	0.310±0.079	0.988	0.058	0.047	10.
64.	ZnI_2	0.276±0.313	-1.724±0.451	1.026±0.114	0.969	0.238	0.050	15.
65.	ZnI_2	-0.104±0.061	-0.966±0.135	0.872±0.077	0.967	0.062	0.066	11.
66.	ZnI_2	-0.547±0.113	-0.220±0.204	0.590±0.088	0.989	0.039	0.041	12.
67.	$Zn(ClO_4)_2$	0.322±0.098	-2.195±0.179	1.943±0.078	0.999	0.032	0.018	10.
68.	$Zn(ClO_4)_2$	0.305±0.078	-2.195±0.139	1.922±0.059	0.999	0.027	0.013	11.
69.	$Zn(ClO_4)_2$	0.326±0.078	-2.193±0.139	1.920±0.059	0.999	0.027	0.013	12.
70.	$Zn(NO_3)_2$	-0.037±0.014	-1.477±0.026	0.959±0.011	0.999	0.005	0.007	10.
71.	$Zn(NO_3)_2$	-0.060±0.009	-1.422±0.015	0.916±0.006	0.999	0.003	0.004	11.
72.	$Zn(NO_3)_2$	-0.061±0.009	-1.419±0.015	0.915±0.006	0.999	0.003	0.004	12.
73.	$Cd(NO_3)_2$	-0.141±0.006	-1.254±0.011	0.627±0.004	0.999	0.002	0.006	10.
74.	$Pb(ClO_4)_2$	0.195±0.062	-2.003±0.103	1.240±0.037	0.998	0.026	0.018	9.
75.	$Pb(ClO_4)_2$	0.121±0.059	-1.865±0.110	1.226±0.051	0.997	0.051	0.027	10.
76.	$Pb(NO_3)_2$	0.049±0.009	-2.073±0.016	0.107±0.007	0.999	0.003	0.002	10.
77.	$Pb(NO_3)_2$	0.087±0.004	-2.132±0.010	0.122±0.006	0.999	0.006	0.002	11.
78.	$FeCl_2$	-0.067±0.009	-1.501±0.016	0.937±0.007	0.999	0.003	0.004	8.
79.	$FeCl_2$	-0.058±0.017	-1.472±0.028	0.917±0.011	0.999	0.006	0.007	10.

Table 1 continued

1	2	3	4	5	6	7	8	9
80.	$FeCl_2$	-0.041±0.013	-1.481±0.022	0.925±0.009	0.999	0.005	0.006	11.
81.	$FeCl_2$	0.005±0.020	-1.355±0.073	1.032±0.069	0.991	0.025	0.051	16.
82.	$CoCl_2$	-0.009±0.007	-1.548±0.012	0.990±0.004	0.999	0.003	0.002	8.
83.	$CoCl_2$	-0.047±0.006	-1.489±0.010	0.952±0.010	0.999	0.002	0.002	10.
84.	$CoCl_2$	-0.017±0.017	-1.538±0.030	0.989±0.012	0.999	0.006	0.007	11.
85.	$CoCl_2$	-0.038±0.007	-1.507±0.012	0.972±0.005	0.999	0.002	0.003	12.
86.	$CoBr_2$	0.304±0.067	-2.141±0.110	1.555±0.038	0.999	0.054	0.013	8.
87.	$CoBr_2$	0.158±0.058	-1.917±0.101	1.465±0.039	0.999	0.022	0.013	10.
88.	$CoBr_2$	0.104±0.038	-1.809±0.067	1.412±0.028	0.999	0.013	0.009	11.
89.	$CoBr_2$	0.104±0.037	-1.806±0.066	1.410±0.026	0.999	0.013	0.009	12.
90.	CoI_2	0.686±0.196	-3.051±0.327	2.356±0.118	0.997	0.081	0.022	8.
91.	CoI_2	0.212±0.058	-2.032±0.099	1.820±0.041	0.999	0.021	0.009	10.
92.	CoI_2	0.070±0.026	-1.702±0.046	1.588±0.019	0.999	0.009	0.005	11.
93.	$Co(ClO_4)_2$	0.131±0.050	-1.761±0.096	1.718±0.048	0.999	0.014	0.012	8.
94.	$Co(NO_3)_2$	-0.033±0.017	-1.537±0.029	0.994±0.011	0.999	0.006	0.008	8.
95.	$Co(NO_3)_2$	-0.006±0.023	-1.565±0.039	0.928±0.015	0.999	0.009	0.010	10.
96.	$Co(NO_3)_2$	-0.036±0.011	-1.501±0.019	0.895±0.008	0.999	0.004	0.006	11.
97.	$NiCl_2$	0.058±0.018	-1.699±0.029	1.082±0.010	0.999	0.008	0.004	8.
98.	$NiCl_2$	0.020±0.022	-1.634±0.038	1.054±0.011	0.999	0.009	0.007	10.
99.	$NiCl_2$	0.011±0.019	-1.604±0.032	1.048±0.013	0.999	0.007	0.007	11.
100.	$NiBr_2$	0.314±0.083	-2.201±0.135	1.680±0.047	0.999	0.034	0.012	8.
101.	$Ni(ClO_4)_2$	0.125±0.049	-1.755±0.094	1.687±0.047	0.999	0.014	0.012	8.

Table 1 continued

1	2	3	4	5	6	7	8	9
102.	$Ni(NO_3)_2$	0.010±0.037	-1.585±0.060	1.005±0.021	0.999	0.016	0.010	8.
103.	$CuCl_2$	-0.273±0.003	-1.062±0.054	0.476±0.021	0.991	0.012	0.040	8.
104.	$CuCl_2$	-0.369±0.053	-0.816±0.080	0.366±0.024	0.989	0.025	0.045	10.
105.	$CuCl_2$	-0.370±0.052	-0.815±0.082	0.313±0.025	0.975	0.025	0.067	9.
106.	$CuCl_2$	-0.232±0.030	-1.128±0.052	0.516±0.021	0.991	0.011	0.039	11.
107.	$CuCl_2$	-0.446±0.096	-0.747±0.176	0.376±0.075	0.851	0.042	0.152	12.
108.	$CuBr_2$	-0.320±0.055	-0.850±0.090	0.711±0.013	0.999	0.024	0.018	9.
109.	$Cu(ClO_4)_2$	0.259±0.075	-2.082±0.135	1.851±0.058	0.999	0.026	0.014	9.
110.	$Cu(NO_3)_2$	0.020±0.028	-1.617±0.046	0.877±0.016	0.999	0.012	0.010	9.
111.	$Cu(NO_3)_2$	-0.087±0.009	-1.420±0.016	0.779±0.007	0.999	0.003	0.007	10.
112.	$Cu(NO_3)_2$	-0.052±0.009	-1.339±0.017	0.747±0.007	0.999	0.003	0.007	11.
113.	$Cu(NO_3)_2$	-0.092±0.007	-1.407±0.013	0.771±0.005	0.999	0.003	0.005	12.
114.	$MnCl_2$	-0.176±0.020	-1.244±0.032	0.741±0.010	0.999	0.009	0.007	9.
115.	$MnCl_2$	-0.341±0.067	-0.898±0.098	0.606±0.025	0.998	0.039	0.017	10.
116.	$MnCl_2$	-0.104±0.013	-1.347±0.023	0.786±0.009	0.999	0.005	0.008	11.
117.	$MnCl_2$	-0.107±0.008	-1.349±0.013	0.779±0.005	0.999	0.003	0.005	12.
118.	$MnBr_2$	0.109±0.030	-1.783±0.049	1.336±0.017	0.999	0.013	0.006	9.
119.	$MnBr_2$	0.065±0.030	-1.718±0.053	1.397±0.022	0.999	0.011	0.007	12.
120.	$Mn(ClO_4)_2$	0.756±0.175	-2.998±0.291	2.444±0.105	0.998	0.074	0.018	9.
121.	Li_2SO_4	-0.008±0.013	-1.661±0.022	0.457±0.007	0.999	0.005	0.011	10.
122.	Na_2SO_4	0.017±0.011	-1.751±0.021	0.231±0.008	0.999	0.005	0.005	10.

Table 1 continued

1	2	3	4	5	6	7	8	9
123.	Na_2SO_4	0.059±0.004	-1.851±0.010	0.247±0.006	0.999	0.006	0.003	11.
124.	K_2SO_4	-0.004±0.019	-1.830±0.046	0.261±0.035	0.999	0.002	0.005	10.
125.	Rb_2SO_4	0.004±0.008	-1.728±0.016	0.262±0.008	0.999	0.002	0.003	10.
126.	Cs_2SO_4	-0.008±0.009	-1.689±0.016	0.300±0.007	0.999	0.003	0.004	11.
127.	Na_2CO_3	-0.030±0.047	-1.561±0.080	0.234±0.029	0.998	0.019	0.021	10.
128.	K_2CO_3	-0.068±0.045	-1.649±0.073	0.533±0.025	0.993	0.012	0.043	10.
129.	Na_2CrO_4	0.029±0.027	-1.700±0.047	0.377±0.018	0.999	0.010	0.015	10.
130.	Na_2CrO_4	-0.017±0.012	-1.604±0.022	0.328±0.009	0.999	0.005	0.006	11.
131.	K_2CrO_4	-0.008±0.018	-1.685±0.030	0.309±0.010	0.999	0.004	0.007	10.
132.	K_2CrO_4	-0.063±0.009	-1.625±0.017	0.289±0.007	0.999	0.003	0.004	11.
133.	$Na_2S_2O_3$	0.030±0.019	-1.762±0.033	0.347±0.013	0.999	0.007	0.009	10.

a) Correlation coefficient

b) Standard deviation

c) Normalized standard error (See [1]).

Table 2

The Results of the Least-Squares Treatment of the Activity Coefficients of 2:I and 1:2 Electrolytes in Aqueous Solutions at 25°C According to Eq.(5).

No	Electrolyte	$\Delta \ln \gamma_{\pm}'$	B_{ij}	r [a]	s [b]	s_o [c]	Reference
1	2	3	4	5	6	7	8
1.	$MgCl_2$	-0.077±0.008	1.046±0.009	0.999	0.016	0.008	10.
2.	$MgCl_2$	-0.011±0.056	1.042±0.005	0.999	0.032	0.011	11.
3.	$MgCl_2$	-0.076±0.006	1.033±0.006	0.999	0.013	0.006	12.
4.	$MgBr_2$	-0.090±0.013	1.318±0.014	0.999	0.024	0.011	10.
5.	$MgBr_2$	-0.010±0.008	1.280±0.009	0.999	0.016	0.007	11.
6.	MgI_2	-0.087±0.025	1.571±0.028	0.999	0.047	0.017	10.
7.	MgI_2	-0.037±0.021	1.575±0.026	0.998	0.036	0.017	11.
8.	MgI_2	-0.095±0.022	1.562±0.022	0.999	0.043	0.014	12.
9.	$Mg(ClO_4)_2$	-0.066±0.023	1.612±0.026	0.999	0.042	0.016	10.
10.	$Mg(ClO_4)_2$	-0.055±0.016	1.551±0.016	0.999	0.032	0.010	11.
11.	$Mg(ClO_4)_2$	-0.055±0.016	1.550±0.016	0.999	0.033	0.011	12.
12.	$Mg(NO_3)_2$	-0.063±0.002	0.963±0.002	0.999	0.004	0.002	10.
13.	$Mg(NO_3)_2$	-0.053±0.003	0.936±0.003	0.999	0.006	0.003	11.
14.	$(CH_3COO)_2Mg$	-0.163±0.003	0.504±0.002	0.999	0.008	0.003	12.
15.	$(CH_3COO)_2Mg$	-0.174±0.001	0.515±0.001	0.999	0.002	0.002	11.
16.	$CaCl_2$	-0.036±0.011	0.869±0.015	0.998	0.035	0.017	10.

Table 2 continued

1	2	3	4	5	6	7	8
17.	$CaCl_2$	0.025±0.007	0.896±0.010	0.999	0.010	0.010	11.
18.	$CaCl_2$	-0.076±0.004	0.898±0.003	0.999	0.007	0.004	12.
19.	$CaBr_2$	-0.089±0.011	1.123±0.013	0.999	0.022	0.011	10.
20.	$CaBr_2$	-0.063±0.030	1.110±0.009	0.999	0.019	0.008	11.
21.	CaI_2	-0.083±0.019	1.362±0.022	0.999	0.036	0.016	10.
22.	CaI_2	-0.090±0.017	1.357±0.018	0.999	0.034	0.013	11.
23.	CaI_2	-0.086±0.016	1.350±0.017	0.999	0.032	0.012	12.
24.	$Ca(ClO_4)_2$	-0.061±0.015	1.349±0.017	0.999	0.028	0.013	10.
25.	$Ca(ClO_4)_2$	0.109±0.048	1.316±0.012	0.999	0.023	0.009	11.
26.	$Ca(NO_3)_2$	-0.084±0.003	0.500±0.003	0.999	0.005	0.006	10.
27.	$Ca(NO_3)_2$	-0.093±0.004	0.492±0.003	0.999	0.007	0.007	11.
28.	$Ca(NO_3)_2$	-0.079±0.003	0.491±0.003	0.999	0.007	0.007	12.
29.	$SrCl_2$	-0.074±0.005	0.831±0.005	0.999	0.009	0.006	10.
30.	$SrCl_2$	-0.073±0.002	0.797±0.002	0.999	0.005	0.003	11.
31.	$SrCl_2$	-0.076±0.004	0.827±0.004	0.999	0.008	0.005	12.
32.	$SrBr_2$	-0.091±0.014	1.029±0.016	0.999	0.027	0.015	10.
33.	$SrBr_2$	-0.091±0.011	1.012±0.011	0.999	0.023	0.011	11.
34.	SrI_2	-0.096±0.024	1.326±0.028	0.998	0.044	0.021	10.
35.	SrI_2	-0.090±0.018	1.285±0.019	0.999	0.036	0.015	11.
36.	SrI_2	-0.096±0.020	1.298±0.021	0.998	0.038	0.016	12.
37.	$Sr(ClO_4)_2$	-0.106±0.010	1.215±0.010	0.999	0.019	0.008	11.
38.	$Sr(NO_3)_2$	-0.079±0.003	0.271±0.002	0.999	0.007	0.008	10.

Table 2 continued

1	2	3	4	5	6	7	8
39.	$Sr(NO_3)_2$	-0.077 ± 0.004	0.274 ± 0.004	0.999	0.008	0.014	11.
40.	$Sr(NO_3)_2$	-0.066 ± 0.008	0.273 ± 0.004	0.998	0.020	0.016	12.
41.	$Sr(NO_3)_2$	-0.083 ± 0.005	0.293 ± 0.005	0.998	0.012	0.016	15.
42.	$BaCl_2$	-0.064 ± 0.002	0.658 ± 0.003	0.999	0.004	0.004	10.
43.	$BaCl_2$	-0.102 ± 0.002	0.671 ± 0.002	0.999	0.004	0.003	11.
44.	$BaCl_2$	-0.064 ± 0.002	0.658 ± 0.002	0.999	0.004	0.003	12.
45.	$BaCl_2$	-0.022 ± 0.012	0.594 ± 0.022	0.988	0.043	0.037	13.
46.	$BaCl_2$	-0.094 ± 0.002	0.654 ± 0.002	0.999	0.003	0.003	14.
47.	$BaBr_2$	-0.079 ± 0.006	0.871 ± 0.007	0.999	0.011	0.008	10.
48.	$BaBr_2$	-0.087 ± 0.005	0.871 ± 0.005	0.999	0.009	0.006	11.
49.	$BaBr_2$	-0.078 ± 0.005	0.862 ± 0.005	0.999	0.009	0.006	12.
50.	BaI_2	-0.108 ± 0.020	1.284 ± 0.024	0.998	0.035	0.018	10.
51.	BaI_2	-0.105 ± 0.016	1.255 ± 0.017	0.999	0.030	0.014	11.
52.	$Ba(ClO_4)_2$	-0.058 ± 0.002	0.925 ± 0.003	0.999	0.004	0.003	10.
53.	$Ba(ClO_4)_2$	-0.058 ± 0.002	0.922 ± 0.002	0.999	0.005	0.003	12.
54.	$Ba(NO_3)_2$	-0.138 ± 0.010	-0.223 ± 0.040	0.985	0.009	0.122	10.
55.	$(CH_3COO)_2Ba$	-0.101 ± 0.015	0.472 ± 0.016	0.993	0.031	0.033	11.
56.	$ZnCl_2$	0.053 ± 0.014	0.331 ± 0.009	0.996	0.033	0.027	10.
57.	$ZnCl_2$	0.061 ± 0.026	0.338 ± 0.028	0.950	0.070	0.078	11.
58.	$ZnCl_2$	0.057 ± 0.017	0.333 ± 0.016	0.985	0.034	0.048	12.
59.	$ZnCl_2$	-0.006 ± 0.009	0.364 ± 0.017	0.983	0.032	0.045	13.

Table 2continued

1	2	3	4	5	6	7	8
60.	$ZnBr_2$	0.199 ± 0.039	0.584 ± 0.021	0.991	0.099	0.035	10.
61.	$ZnBr_2$	0.100 ± 0.031	0.733 ± 0.033	0.987	0.070	0.044	11.
62.	$ZnBr_2$	0.121 ± 0.036	0.719 ± 0.036	0.984	0.072	0.049	12.
63.	ZnI_2	0.235 ± 0.064	0.911 ± 0.049	0.983	0.143	0.053	10.
64.	ZnI_2	0.096 ± 0.097	0.960 ± 0.032	0.986	0.235	0.032	15.
65.	ZnI_2	0.096 ± 0.032	1.133 ± 0.036	0.992	0.082	0.032	11.
66.	ZnI_2	0.126 ± 0.038	1.103 ± 0.040	0.992	0.075	0.036	12.
67.	$Zn(ClO_4)_2$	-0.079 ± 0.028	1.628 ± 0.031	0.998	0.053	0.019	10.
68.	$Zn(ClO_4)_2$	-0.108 ± 0.024	1.616 ± 0.025	0.999	0.048	0.015	11.
69.	$Zn(ClO_4)_2$	-0.085 ± 0.024	1.615 ± 0.025	0.999	0.048	0.015	12.
70.	$Zn(NO_3)_2$	-0.051 ± 0.003	0.949 ± 0.003	0.999	0.005	0.003	10.
71.	$Zn(NO_3)_2$	-0.044 ± 0.002	0.928 ± 0.002	0.999	0.003	0.002	11.
72.	$Zn(NO_3)_2$	-0.044 ± 0.002	0.927 ± 0.002	0.999	0.003	0.002	12.
73.	$Cd(NO_3)_2$	-0.031 ± 0.007	0.703 ± 0.006	0.999	0.013	0.009	10.
74.	$Pb(ClO_4)_2$	-0.132 ± 0.019	1.047 ± 0.015	0.998	0.043	0.014	8.
75.	$Pb(ClO_4)_2$	-0.097 ± 0.015	1.040 ± 0.019	0.998	0.028	0.018	10.
76.	$Pb(NO_3)_2$	-0.285 ± 0.019	-0.159 ± 0.022	0.923	0.036	0.128	10.
77.	$Pb(NO_3)_2$	-0.171 ± 0.036	-0.270 ± 0.041	0.854	0.093	0.130	11.
78.	$FeCl_2$	-0.095 ± 0.002	0.917 ± 0.002	0.999	0.004	0.002	9.
79.	$FeCl_2$	-0.070 ± 0.003	0.909 ± 0.003	0.999	0.006	0.003	10.
80.	$FeCl_2$	-0.059 ± 0.002	0.913 ± 0.002	0.999	0.005	0.003	11.
81.	$FeCl_2$	0.029 ± 0.010	1.116 ± 0.028	0.998	0.026	0.024	16.

Table 2 continued

1	2	3	4	5	6	7	8
82.	$CoCl_2$	-0.068 ± 0.003	0.960 ± 0.002	0.999	0.008	0.002	8.
83.	$CoCl_2$	-0.068 ± 0.002	0.947 ± 0.001	0.999	0.003	0.002	10.
84.	$CoCl_2$	-0.067 ± 0.004	0.954 ± 0.004	0.999	0.008	0.004	11.
85.	$CoCl_2$	-0.071 ± 0.002	0.950 ± 0.002	0.999	0.004	0.002	12.
86.	$CoBr_2$	-0.111 ± 0.023	1.324 ± 0.017	0.999	0.054	0.013	8.
87.	$CoBr_2$	-0.106 ± 0.019	1.291 ± 0.017	0.999	0.038	0.013	10.
88.	$CoBr_2$	-0.095 ± 0.012	1.267 ± 0.012	0.999	0.024	0.009	11.
89.	$CoBr_2$	-0.095 ± 0.012	1.266 ± 0.012	0.999	0.023	0.010	12.
90.	CoI_2	-0.257 ± 0.056	1.794 ± 0.044	0.995	0.127	0.024	8.
91.	CoI_2	-0.112 ± 0.021	1.595 ± 0.020	0.999	0.042	0.013	10.
92.	CoI_2	-0.071 ± 0.008	1.487 ± 0.008	0.999	0.017	0.005	11.
93.	$Co(ClO_4)_2$	-0.028 ± 0.012	1.569 ± 0.015	0.999	0.020	0.010	8.
94.	$Co(NO_3)_2$	-0.081 ± 0.004	0.901 ± 0.004	0.999	0.008	0.004	8.
95.	$Co(NO_3)_2$	-0.065 ± 0.002	0.874 ± 0.002	0.999	0.005	0.003	11.
96.	$Co(NO_3)_2$	-0.070 ± 0.006	0.086 ± 0.005	0.999	0.011	0.006	10.
97.	$NiCl_2$	-0.093 ± 0.008	1.004 ± 0.006	0.999	0.019	0.006	8.
98.	$NiCl_2$	-0.085 ± 0.007	0.988 ± 0.007	0.999	0.015	0.007	10.
99.	$NiCl_2$	-0.076 ± 0.005	0.987 ± 0.005	0.999	0.011	0.005	11.
100.	$NiBr_2$	-0.093 ± 0.008	1.358 ± 0.019	0.998	0.061	0.014	8.
101.	$Ni(ClO_4)_2$	-0.032 ± 0.012	1.542 ± 0.015	0.999	0.020	0.009	8.
102.	$Ni(NO_3)_2$	-0.064 ± 0.006	0.953 ± 0.004	0.999	0.013	0.005	8.

Table 2 continued

1	2	3	4	5	6	7	8
103.	$CuCl_2$	-0.050±0.013	0.621±0.011	0.998	0.027	0.019	8.
104.	$CuCl_2$	0.026±0.026	0.551±0.016	0.995	0.062	0.029	10.
105.	$CuCl_2$	0.025±0.026	0.500±0.016	0.944	0.061	0.033	9.
106.	$CuCl_2$	-0.052±0.010	0.624±0.010	0.998	0.021	0.016	11.
107.	$CuCl_2$	-0.029±0.011	0.632±0.011	0.998	0.023	0.017	12.
108.	$CuBr_2$	0.041±0.020	0.913±0.015	0.998	0.046	0.016	9.
109.	$Cu(ClO_4)_2$	-0.087±0.022	1.587±0.023	0.999	0.042	0.015	9.
110.	$Cu(NO_3)_2$	-0.080±0.007	0.822±0.005	0.999	0.016	0.007	9.
111.	$Cu(NO_3)_2$	-0.070±0.002	0.792±0.002	0.999	0.003	0.002	10.
112.	$Cu(NO_3)_2$	-0.060±0.004	0.791±0.003	0.999	0.007	0.004	11.
113.	$Cu(NO_3)_2$	-0.068±0.002	0.788±0.002	0.999	0.004	0.002	12.
114.	$MnCl_2$	-0.050±0.007	0.808±0.005	0.999	0.017	0.006	9.
115.	$MnCl_2$	0.015±0.026	0.742±0.012	0.998	0.070	0.017	10.
116.	$MnCl_2$	-0.046±0.003	0.825±0.004	0.999	0.008	0.004	11.
117.	$MnCl_2$	-0.051±0.003	0.819±0.003	0.999	0.006	0.004	12.
118.	$MnBr_2$	-0.089±0.011	1.224±0.008	0.999	0.025	0.007	9.
119.	$MnBr_2$	-0.081±0.009	1.290±0.009	0.999	0.018	0.007	12.
120.	$Mn(ClO_4)_2$	-0.150±0.057	1.904±0.041	0.996	0.120	0.022	9.
121.	Li_2SO_4	-0.131±0.008	0.388±0.006	0.999	0.017	0.015	10.
122.	Na_2SO_3	-0.173±0.012	0.103±0.011	0.949	0.025	0.099	10.

Table 2 continued

1	2	3	4	5	6	7	8
123.	Na_2SO_4	-0.097 ± 0.020	0.032 ± 0.022	0.333	0.057	0.229	11.
124.	K_2SO_4	-0.163 ± 0.009	-0.023 ± 0.024	0.432	0.009	0.450	10.
125.	Rb_2SO_4	-0.138 ± 0.008	0.130 ± 0.011	0.971	0.014	0.084	10.
126.	Cs_2SO_4	-0.135 ± 0.007	0.193 ± 0.008	0.991	0.012	0.039	11.
127.	Na_2CO_3	-0.093 ± 0.009	0.195 ± 0.008	0.992	0.019	0.040	10.
128.	K_2CO_3	-0.195 ± 0.008	0.464 ± 0.007	0.999	0.016	0.015	10.
129.	Na_2CrO_4	-0.113 ± 0.010	0.285 ± 0.009	0.995	0.020	0.031	10.
130.	Na_2CrO_4	-0.104 ± 0.005	0.267 ± 0.005	0.998	0.010	0.018	11.
131.	K_2CrO_4	-0.148 ± 0.007	0.227 ± 0.006	0.997	0.012	0.026	10.
132.	K_2CrO_4	-0.169 ± 0.003	0.225 ± 0.003	0.999	0.005	0.012	11.
133.	$Na_2S_2O_3$	-0.146 ± 0.011	0.231 ± 0.010	0.991	0.022	0.043	10.

(a-c
See corresponding footnotes at Table 1.

Table 3.

Recommended $B_{ij(1:1)} = 2V_s$ Values for 2:1 Electrolytes in Aqueous Solutions at 25°C (l/mol)

Anion / Cation	Cl^-	Br^-	I^-	NO_3^-	ClO_4^-
Mg^{2+}	0.520	0.649	0.785	0.473	0.786
Ca^{2+}	0.448	0.557	0.678	0.248	0.664
Sr^{2+}	0.409	0.510	0.649	0.138	0.608
Ba^{2+}	0.327	0.433	0.632	-0.111	0.463
Zn^{2+}	0.167	0.362	0.513	0.474	0.809
Co^{2+}	0.478	0.638	0.798	0.443	0.785
Ni^{2+}	0.497	0.679	-	0.477	0.771
Cu^{2+}	0.293	0.457	-	0.411	0.794
Mn^{2+}	0.409	0.629	-	-	0.952
Pb^{2+}	-	-	-	-0.106	0.522

The recommended values of $B_{i(1:1)}$ are given in Table 3.

In the previous communication[2] the existence of simple linear relationship between the parameters

$$\Delta B_{ij} = B_{ij} - B_{oj} , \qquad (8)$$

(where j stands for the anion index, i and 0 denote the cation in given series and the reference cation, correspondingly), and anionic crystallographic radiuses r_j was pointed out. The analogous relationships seem to be approximately valid within a quite restricted choice of bivalent cations. (See Fig. 2.), and namely, for Mg-, Ca- and Sr - salts. In the case of Ba- and bivalent transient metal salts there is no regular dependence between the values of ΔB_{ij} and corresponding crystallographic radiuses r_j.

Therefore, the structural dependence of B_{ij}-parameters of electrolytes of different charge types in aqueous solutions need a special discussion which will be published elsewhere.

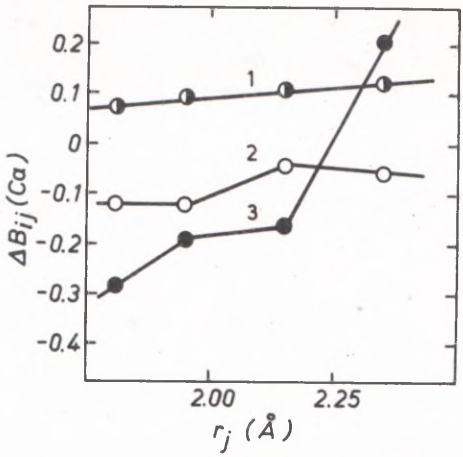

Fig. 2. The relationship between the ΔB_{ij}-parameters (Eq.8) and the anion crystallographic radiuses r_j. (Ca - salts taken as reference). 1-Mg^{2+}, 2-Ba^{2+}, 3-Zn^{2+}

References.

1. M.M. Karelson, This journal, 21, 160(1984)
2. M.M. Karelson and T. Sepp, This journal, 21, 328(1984)
3. H. Frank and D.T.Thompson, Ch.8. in "The Structure of Electrolyte Solutions," Ed. W.J. Hamer, J. Wiley and Sons, New York, 1959.
4. J.E. Desnoyers and B.E. Conway, J.Phys.Chem., 68,(8), 2305(1964)
5. L. Bähe, J.Phys.Chem., 76,(7),1062(1972)
6. E.M. Kuznetsova, Dokl. AN SSSR, 264,(2) 360(1982)
7. R. Robinson and R.A. Stokes, Electrolyte Solutions, Butterworths, London, 1959
8. R.N. Goldberg, R.L. Nuttall, and B.R. Staples, J.Phys. Chem. Ref. Data, 8, (4), 923(1979).
9. R.W. Goldberg, J.Phys.Chem.Ref.Data, 8, (4),1005 (1979)
10. Handbook of Electrochemistry (in Russian), Ed.A.M.Sukhotin, Leningrad, 1981

11. D. Dobos, Electrochemical Data, Akad.Kiado, Budapest,1975
12. I.E. Voznesenskaya, in : "The Problems of Physical Chemistry of Electrolyte Solutions" (in Russian) "Khimija" Leningrad, 1968, p. 172
13. G. Scatchard and R.F. Tefft, J. Amer.Chem.Soc., 52,(6), 2272 (1930)
14. R.A. Robinson, J. Amer.Chem.Soc, 59,(1), 84(1937)
15. M. Randall and M. Frandsen, J. Amer.Chem.Soc., 54,(1), 47(1932)
16. W. Kangro and A. Groeneveld, Z.phys.Chem., NF, 32,110 (1962).

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ION DISTRIBUTION IN ELECTROLYTE SOLUTIONS.

M.M. Karelson

Laboratory of Chemical Kinetics and Catalysis, Tartu State University, Tartu 202400 Estonian S.S.R. USSR

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A new ion distribution function around a reference ion in the electrolyte solutions is derived. This distribution function is energetically consistent with the quasi-lattice theory of solutions, but does not include any assumptions about the long-range structure of solution. The actual form of this function is similar to the well-known Boltzmann distribution function of charged particles in external electric field, characterized by the potential f :

$$n = n_o \exp(- ze f /\beta),$$

where n is the space density of particles with the charge ze, and n_o is their bulk stochiometric density. Only the scaling factor β has a different meaning, and it is equal to the electrostatic interaction energy of electrolyte constituent counterions at the average nearest-neighbour distance between them at a given concentration of solution.

The correlation functions between constituent particles play a key role in the theory of liquids and solutions.[1,2] The pair correlation function, or the radial distribution function in case of central field potentials are the most important of them in the determination of the thermodynamic

properties of solutions. This is also true for the electrolyte solutions, where the longrange interionic electrostatic forces are the main factors determining the structure of the system.

A number of valuable rigorous statistical-mechanical investigations of simple model systems referring to the electrolyte solutions have been made during last decades. They include the integral equation approaches using mean spherical approximation[3,4], hypenetted chain,[5-7] Percus-Yevick[8] and Born-Green-Yvon[9] theories but also the cluster expansion techniques[10-12]. The excellent computer experiments on model electrolyte systems have been carried out with Monte Carlo[13-15] and molecular dynamics[16] programs. Macroscopic solution theory has been improved by the use of nonlocal screening concept[17]. However, the general problem connected with the statistical physics of liquid state enforce often the use of very crude approximations of the real systems. Therefore there is a constant interest in simpler statistical theories of the electrolyte solutions with the accent on the interionic electrostatic interactions.[18]

The most eloquent of these simple theories is indeed the historically prime Debye-Hückel theory[19,20]. In the original form it approximates the electrolyte solution with the system of oppositely charged mass points in the homogeneous medium characterized by the macroscopic dielectric constant. However, the internal restrictions of this theory, regardless of the further improvements taking into account the finete size of ions[21] or dielectric saturation around them[22] make it suitable only at limiting dilutions.[23-25]

Alternatively a number of authors[26-35] have recently emphazised the usefulness of the quasilattice theory of electrolyte solutions for the description of their thermodynamic properties in large concentration limits. In the framework of this theory the electrostatic free energy of 1 mole of electrolyte in solution is presented by the following equation

$$\Delta G_{el} = \frac{A_M (z_+ e)(z_- e)}{\varepsilon \cdot \bar{I}} N_A \quad , \qquad (1)$$

where z_+e and z_-e are the charges of cation and anion, respectively, $\mathcal{E}$ is the macroscopic dielectric constant of the solvent, N_A - the Avogadro numbers, and $\bar{l}$ is the average distance between the nearest-neighbour ions at the absolutely uniform distribution of them in solution. The constant A_M has usually the meaning of the Madelung' constant for the simplest lattice of the given electrolyte type. The essential weak point of the quasi-lattice theory is indeed the assumption of strong long-distance order in solution which is not confirmed by the independent scattering experiments.

The more realistic ion distribution about the reference ion is given by the electrostatic Poisson equation

$$\nabla^2 \varphi = -\frac{4\pi}{\mathcal{E}} \rho \qquad (2)$$

where φ denotes the electric potential and ρ is the excess space-charge density. The latter refers actually to a continuous charge distribution whereas it is caused by the oppositely charged discrete ions in equilibrium state (at infinitely long time of exploration):

$$\rho = z_+ e n_+ + z_- e n_- , \qquad (3)$$

In this formula, n_+ and n_- are the space densities of cations and anions correspondingly. The main difficulty which now arises in the original Debye-Hückel treatment, is the use of Boltzmann distribution function in the calculation of space densities n_+ and n_- of ions:

$$n_\pm = n_{o(\pm)} \exp(-z_\pm e\varphi /kT), \qquad (4)$$

where $n_{o(\pm)}$ is the bulk space density of respective ions in solution and kT is the Boltzmann factor. There is much criticism about the fact that the Boltzmann distribution function does not satisfy the main electrostatic theorem about the superposition of potentials, i.e. the charge density in a space point is the exponential function of φ , but not the linear one[18,24-25]. We should like to emphasize another questionable point of the use of the Boltzmann distribution (4) for the ions around a reference ion: the origin of the

coordinates is located on the reference (central) ion and the movement of other ions is observed relative to this fixed point. Consequently, the thermodynamic system, which consists of the ions interacting with the central ion (ion atmosphere) contains only a few of them. Therefore, the use of statistical Boltzmann distribution for charged particles in the external electric field is not justified as the number of particles for the statistical approach has to be much greater (10^{10}-10^{15}). On the other hand, such a system must be of quasi-quantum nature in the stationary state because according to the general principles of classical electrodynamics the set of static or dynamic charges in equilibrium is impossible. This is also against the use of Eq. (4) for the ion distribution function.

There have been attempts to use other distribution functions accounting the finite size of ions in ion atmosphere,[36] the ion-pairing[37,38] or quantum effects[39], but without any apparent success when compared with experimental results.

In the present communication we propose to use a modified Boltzmann distribution which would be consistent with the quasi-lattice theory results about the excess free energy of electrolyte in solution[35,40]. In other aspects the model of ionic solution is identical with the original Debye-Hückel-Milner model,[19,20] i.e. the point charges are investigated in a homogeneous dielectric medium. The distribution of ions of given charge at the space point characterized by the electrostatic potential φ is presented by the following equation:

$$n_{\pm} = n_{o(\pm)} \exp(-z_{(\pm)} e \varphi / \beta) \quad , \qquad (5)$$

where β is some (at this point unknown) scaling factor. The determination of the actual form of this scaling factor is the subject of our further discussion.

For the sake of simplicity the case of symmetrical electrolytes (1:1, 2:2 etc) is considered first. Then

$$z_+ = -z_- = z \text{ and } n_{o(+)} = n_{o(-)} = n_o$$

and the corresponding distribution functions (5) around a reference cation are given as:

$$n_+ = n_0 \exp(-ze\varphi/\beta) \qquad (5a)$$

and

$$n_- = n_0 \exp(ze\varphi/\beta). \qquad (5b)$$

It has to be underlined, that the functions n_+ and n_- describe the distribution of corresponding ions in respect to their potential energies in the field of central ion, i.e.

$$n_+ = n_+(ze\varphi)$$

and

$$n_- = n_-(-ze\varphi)$$

essentially. On the other hand, the Maxwell-Boltzmann distribution deals with the collision energy between particles, i.e.

$$n = n(mv^2)$$

The energy scaling factor in this distribution is the mean collision energy between particles in the given system and it is determined by the thermodynamic temperature of the system as kT, where k is the Boltzmann constant. We can obviously assume that the scaling factor in the distributions (5) is connected with some average electrostatic potential energy of ions in solution. The energy between the oppositely charged ions at the average distance $\bar{l}$ between them:

$$\beta = \frac{(ze)^2}{\varepsilon \bar{l}} \qquad (5c)$$

is the natural parameter to use of scaling factor β.
The excess space-charge density is now

$$\rho = zen_0\left[\exp(-ze\varphi/\beta) - \exp(ze\varphi/\beta)\right] \qquad (6)$$

The exponential linearization approximation made in original Debye-Hückel treatment has to be made here also, i.e.:

$$\exp(\pm ze\varphi/\beta) = 1 \pm ze\varphi/\beta. \qquad (7)$$

However, as we like to show in further discussion, the loss of precision due to this assumption is of less order than in the Debye-Hückel treatment and depends on the nature of scaling factor β.

Then the excess space-charge density around some ion (for the further discussion, cation) is given by the following formula:

$$\rho = -\frac{2n_o(ze)^2\varphi}{\beta} = \text{const.}\,\varphi \qquad (8)$$

which is now linearity relation with the electrostatic potential φ in solution. By giving to the const in the last equation another form using the parameter $\varkappa^2$, we get as a result

$$\rho = -\frac{\varkappa^2\varepsilon}{4\pi}\varphi \qquad (9)$$

The right side of this formula can be substituted into the Poisson equation (2), which gives the usual linearized Poisson equation:

$$\nabla^2\varphi = \varkappa^2\varphi \qquad (10)$$

The physically meaningful solution of this differential equation in the case of central field potential is as follows[19]:

$$\varphi = A\frac{e^{-\varkappa r}}{r}\,, \qquad (11)$$

where r is the distance from the origin (reference ion). The unknown coefficient A is found from the total electroneutrality condition of the solution. The excess charge density ρ is presented by the substitution of Eq. (11) into Eq. (9) as

$$\rho = -\frac{A\varkappa^2\varepsilon}{4\pi}\cdot\frac{e^{-\varkappa r}}{r} \qquad (12)$$

From the total electroneutrality limiting condition it follows that the integral

$$Q = \int_V \rho dv = 4\pi\int_0^\infty \rho r^2 dr = A\varkappa^2\varepsilon\int_0^\infty e^{-\varkappa r} r dr = -ze, \qquad (13)$$

i.e. the total excess charge in ion atmosphere Q has to be equal to the opposite value of central ion charge. After

integration of the left side of the last equation we get the following value for constant A:

$$A = -\frac{ze}{\varepsilon} \qquad (14)$$

This is exactly the result obtained in the original Debye--Hückel theory. However, the other unknown constant in the expressions of φ and ρ, parameter $\varkappa$, has a different meaning in our approach.

By comparison of the Eq.-s (5^c,8,9) the value of $\varkappa$ is simply

$$\varkappa = \frac{2\sqrt{\pi}}{I} \qquad (15)$$

We derive now the formula for the mean electrostatic free energy for the electrolyte solution from (cf. Eq.(1)). Let us define the electrostatic excess free energy of one (arbitrary) ion in solution as u. In the case of symmetrical electrolyte this energy is the same for cations and anions, indeed. Therefore the electrostatic excess free energy of 1 mole electrolyte in solution is

$$\Delta G_{el} = (N_A \cdot u + N_A \cdot u)/2 = N_A \cdot u \qquad (16)$$

The electrostatic excess free energy of an ion can be found from the charge distribution around it. We use here the simple and illustrative method where this quantity is calculated, as a sum of two terms. The former takes into account the electrostatic energy of ion interaction with ion atmosphere and the latter is the ion atmosphere formation formation energy.[*]

$$u = 4\pi\int_0^\infty \frac{ze\,\rho(r)}{\varepsilon\, r}\, r^2 dr + \frac{16\pi^2}{\varepsilon}\int_0^\infty \rho(a)a^2 da\left\{\frac{1}{a}\int_0^a \rho(r)r^2 dr + \int_a^\infty \frac{\rho(r)r^2 dr}{r}\right\} = -\frac{(ze)^2\varkappa}{\varepsilon} + \frac{(ze)^2\varkappa}{2\varepsilon} = -\frac{(ze)^2\varkappa}{2\varepsilon} \qquad (17)$$

[*] There is a number of other methods[19,41,42] to estimate this electrostatic excess free energy of ion in solution, but all of them give the same result.

Consequently, the electrostatic excess free energy of 1 mole of electrolyte is as follows:

$$\Delta G_{el} = N_A \cdot u = - N_A \cdot \frac{(ze)^2 \varkappa}{2\varepsilon} = - N_A \frac{(ze)^2 \sqrt{\pi}}{\varepsilon \bar{l}} \quad (18)$$

which is now uniquely determined by the concentration of electrolyte in solution if to keep in mind that the mean space density which corresponds to it

$$n_o = \frac{1}{2\bar{l}^3} \quad (19)$$

is simply related to the characteristic nearest-neighbor distance, $\bar{l}$, and by the theoretical constants.

It is now comparatively simple to proceed analogous derivation of the partial excess electrostatic free energy of ions in solution for the unsymmetrical electrolytes. The following general formula for the electrostatic excess free energy in solution for the electrolyte $A_{\nu_+}^{z+} B_{\nu_-}^{z-}$:

$$\Delta G_{ex}(el.) = \frac{N_A \cdot (\nu_+ + \nu_-) \sqrt{\pi}}{2} \cdot \frac{z_+ z_- e^2}{\varepsilon \bar{l}} =$$

$$= \frac{24.7689}{\varepsilon} z_+ z_- (\nu_+ + \nu_-) \sqrt[3]{\nu c} \quad (20)$$

is valid, where ν is the total number of ions in electrolyte ($\nu = \nu_+ + \nu_-$) and c - the molar concentration of electrolyte in solution.

For the electrostatic part of the mean activity coefficient of an ion having a charge of absolute value ze, the following equation is valid respectively:

$$\ln f_{z(el)} = - \frac{(ze)^2 \varkappa}{4\varepsilon RT} = - \frac{12464.2 z^2}{\varepsilon T} \sqrt[3]{\nu c}, \quad (21)$$

where ε is the macroscopic dielectric permittivity of the solvent and T is the absolute temperature (^oK).

It is simple to see, that the form of concentrational dependence of $\Delta G_{ex}(el)$ (20) is identical to that obtained from the semi-empirical quasi-lattice theory (cf. Eq. (1)). The coefficient A_M is, however, fully theoretical and does not

depend on the assumption about some (long-range) order in solution. The data, given in Table, summarize the A_M values obtained from the Eq.(20), their "experimental" values obtained from the slopes of the dependence of the experimental partial excess free energies on the cuberoot of electrolyte concentration, and Madelung constants for the electrolytes of given charge type. It can be seen that the A_M

Table

The Value of the Parameter A_M Obtained by the Different Approaches

Electrolyte type	A_M values		
	Lattice theory	Eq. (20)	experimental
1 : 1	1.748(NaCl)	$\sqrt{\pi}$ = 1.7724	1.750±0.033
2 : 1	2.502(CaF_2)	$\frac{3}{2}\sqrt{\pi}$ = 2.6586	2.634±0.052
3 : 3	3.322(AlF_3)	$2\sqrt{\pi}$ = 3.5548	3.497±0.046

values obtained from different sources, are close to one another with slightly better agreement between the experimental results and the theoretical quantities obtained in this work. Therefore, only the diminishing of empirical parameters practically to zero makes the approach presented in this work superior to the quasi-lattice theory for the description of strong electrolyte solutions.

In the end we should like to emphasize, that the result obtained in this work is quite problematic, for the Boltzmann distribution function is changed in a not common way. However, we feel intuitively that for the quantum (or quasi-quantum) system which seems to be the case of strong electrolytic solutions, the energy scaling factor in the distribution function of the particles in external potential field has to be connected with some characteristic potential energy of the particles instead of their kinetic energy.

Therefore it should be of general theoretical interest to investigate into such systems starting from the vigorous statistical mechanics at the very origin. The main objective for this is the questionable fact that the use of distribution functions in a given above way enables to link the sim-

plest electrostatistical model of the ionic solutions with the experimental data in the wide region of the observable change.

References

1. C.A. Croxton, Liquid State Physics - A Statistical Mechanical Introduction, Cambridge University Press, 1974.
2. R.P. Feynman, Statistical Mechanics, W.A. Benjamin, Inc., Reading, Mass., 1972
3. E. Waisman and J.L. Lebowitz, J. Chem. Phys., 52, 4307 (1970)
4. L. Blum, Theor. Chem. Adv. and Perspect, 5,1(1980)
5. J.C. Rassaiah, J. Solut. Chem., 2, 301(1973)
6. D.D. Carley, J. Chem. Phys., 46, 3783 (1967)
7. G.N. Patey, Mol. Phys., 34, 427 (1977)
8. A.R. Allnatt, Mol. Phys., 8, 533 (1964)
9. T.L. Croxton and D.A. McQuarrie, J. Phys. Chem., 83, 1840 (1979)
10. H.C. Andersen and D. Chandler, J. Chem. Phys., 57, 1918 (1972)
11. G. Stell, J. Chem. Phys., 59, 3926 (1973)
12. L.L. Friedman, Ionic Solution Theory, Interscience-Wiley, New-York, 1964
13. J.C. Poirier, Ch. 2 in: "Chemical Physics of Ionic Solutions," Eds. B.E. Conway and R.G. Barradas, J. Wiley & Sons, Inc.,New York, 1966
14. D.N. Card and J.P. Valleau, J. Chem. Phys., 52, 6232 (1970)
15. J.P. Valleau and L.K. Cohen, J. Chem. Phys., 72, 5935 (1980)
16. K. Heinziger and P.C. Vogel, Z. Naturforsch., 31a, 463 (1976)
17. A.A. Kornyshev, Electrochim. Acta, 26, 1 (1981)
18. B.E. Conway, Compr. Treat. Electroohem., 5, 111(1983)
19. P. Debye and E. Hückel, Phys. Z., 24, 185 (1923)

20. S.R. Milner, Phil. Mag., 23, 551 (1912)
21. E. Hückel, Phys. Z., 26, 93 (1925)
22. K. Holub and A.A. Kornyshev, Z. Naturforsch., 31a, 1601 (1976)
23. H.S. Frank and P.T. Thompson, Ch. 8 in Structure of Electrolytic Solutions," Ed. W.J. Hamer, J. Wiley and Sons, New York, 1959
24. B.E. Conway, Introduction in "Chemical Physics of Ionic Solution, Eds. B.E. Conway and R.G. Barradas, J. Wiley and Sons, Inc., New York, 1966
25. H.C. Andersen, Mod. Aspects Electrochem., 11, 1; (1975)
26. H.S. Frank and P.T. Thompson, J. Chem. Phys., 31,1086 (1959)
27. J.E. Desnoyers and B.E. Conway, J. Phys. Chem., 68, 2305 (1964)
28. L. Bahe, J. Phys. Chem., 76, 1062 (1972)
29. I. Ruff, J. Chem. Soc. Farad. Trans., II, 73, 1858 (1977)
30. I. Ruff, K. Gombos and G. Palinkas, Magy. Kem. Foly., 88, 7 (1982)
31. T. Hurlen, Acta Chem. Scand., A35, 587 (1981)
32. G.W. Murphy, J. Chem. Soc. Farad. Trans., II, 78, 881 (1982)
33. J. Nanda, Proc. Indian Natn. Sci. Acad., 48A 584(1982)
34. E.M. Kuznetsova, Dokl. AN SSSR, 264, 360 (1982)
35. M.M. Karelson, Organic Reactivity, 21, 160 (1984)
36. M. Eigen and E. Wicke, Naturwissenschaften, 38, 453(1951), 39, 545 (1952)
37. T.H. Stillinger and R.J. White, J. Chem. Phys., 54, 3405 (1971)
38. R.J. Wheaton, J. Chem. Soc. Farad. Trans. II, 76, 1599 (1980)
39. S.N. Bagchi, J. Indian Chem. Soc., 27, 199 (1950)
40. M.M. Karelson and T. Sepp, Organic Reactivity, 21, 320 (1984)
41. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworths, London, 1959
42. E. Guntelberg, Z. phys. Chem., 123, 199 (1926)
43. M.M. Karelson, Organic Reactivity,22, (in press).(1985).

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LINEAR FREE ENERGY RELATIONSHIPS OF THE ION-SOLVENT INTERACTION PARAMETERS

M.M. Karelson
Laboratory of Chemical Kinetics and Catalysis, Tartu State University, Tartu 202400 Estonian S.S.R.

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The analysis of the solvent structurization parameters V_s for electrolytes in aqueous solutions[1,2] on the ground of their linear relationships with the intrinsic energetic characteristics of the electrolyte constituent ions has been proposed. It has been shown that for both cations and anions a substantial contribution from the solvent electrostatic polarization energy according to Born is present in V_s. In the case of anions there is an additional effect connected with the hydrogen - bond formation free energy between the anions and water molecules as hydrogen bond donors.

The comparison with the results of the earlier treatment of analogous ion - solvent interaction parameters has also been made.

The description of the partial molar excess free energy of electrolyte in solution $\Delta G_{ex} = \nu RT \ln f_{\pm}$ is of main importance in the physical chemistry of solutions. Recently it has been emphasized[1-3] that the concentration dependence of ΔG_{ex} can be presented as the sum of two independent contributions:

$$\Delta G_{ex} = \Delta G_{ii} + \Delta G_{is} \qquad (1)$$

where ΔG_{ii} represents the purely interionic interaction free energy and ΔG_{is} is the partial excess free energy of electrolyte caused by the ion - solvent interaction. According to the structural model of the solution accepted in papers[1-3], the first term ΔG_{ii} has the following form:

$$\Delta G_{ii} = \frac{A_M z_c z_a^* \alpha}{\varepsilon} \sqrt[3]{c} \qquad (2)$$

where c is the molar concentration of the solution, z_c and z_a the ionic charges of cation and anion, respectively, ε - the macroscopic dielectric constant of the solvent and A_M - the structural constant, which is characteristic of the electrolyte of a given charge type. The coefficient α is the free energy scaling factor, and depends only on the choice of the energy and concentration units. In quasi - lattice models[1,3,5-8] of the electrolyte solution the constant A_M is considered to have the content of the Madelung constant for a given lattice type. However, it has been shown recently[9], that this constant could be calculated from the simple Milner - Debye - Hückel model of ionic solutions with the modified ion distribution function, and there are no assumptions about the long - range order between ions. The second term in Eq. (1) has the linear dependence on the electrolyte concentration c in solution[1]:

$$\Delta G_{is} = 2\nu RTV_s c \quad , \qquad (3)$$

where V_s is the specific volume of solvent restructurization by a given electrolyte, and ν is the number of ions in the molecule of the latter. The V_s parameter is numerically equal to the volume around the 1 mole of ions, where the solvent molecules are transferred from the unperturbed state corresponding to the pure solvent at a given temperature to the totally ordered state (according to the two-state theory of liquids[20,11]). The negative values of the V_s refer to the total disordering of the solvent in this volume.

The validity of the above-given model in a wide range of concentrations (0 - 6 M) was demonstrated on the basis of the experimental data of a number of 1:1-, 2:1- and 1:2-electrolytes elsewhere[2,4]. The multiple and linear correlation coefficients were $r > 0.99$, and the standard deviations $s \leq 0.05$ kJ/mol.

Therefore, the partial molar excess free energy of electrolyte solutions has two principally different terms. The electrostatic term ΔG_{ii} is substantially non-specific of a particular electrolyte and depends only on its charge type. Consequently, the electrostatic excess free energy of a electrolyte in solution of a given concentration is a constant for all the electrolytes of this charge type. On the other hand, the second term ΔG_{is} is highly specific for every electrolyte due to the differences in the V_s-parameter. The V_s of the electrolyte is therefore the only parameter, which determines the individuality of the partial excess molar free energy of electrolyte in solution, and its activity coefficient, too. Consequently, it is important to derive the dependence of V_s-parameters on the intrinsic structural factors of the corresponding salts.

The numerical values of the specific volumes V_s for the most representative series of 1:1- and 2:1- electrolytes are given in Table 1. It is interesting to note the existence of approximate correlations between the V_s- parameters and ion-solvent interaction parameters β , obtained in the extended Debye - Hückel type theories by Guggenheine and Turgeon[12,13] and Pitzer[14] (see Fig. 1 and 2.). This is only due to the similarity of corresponding terms ΔG_{is}, which is the main factor in partial excess free energy of electrolyte of concentrated solutions. In the further discussion we restrict ourselves to the discussion of the V_s-values, bearing in mind their approximate linearity from other ion-solvent interaction parameters. The V_s-parameters given in Table 1 can be formally divided into cationic and anionic parts. Then

$$V_{s(ij)} = V_{s(ij)}\,(\text{cation}) + V_{s(ij)}(\text{anion}) \qquad (4)$$

in case of 1:1 - electrolytes and

Table 1

The Parameters of Solvent Structurization V_s For 1:1[3] and 1:2[4] Electrolytes at 25°C in Aqueous Solutions (l/mol).

Cation \ Anion	F^-	Cl^-	Br^-	I^-	OH^-	CH_3COO^-	NO_3^-	ClO_4^-
Li^+		0.202	0.238	0.281	0.043	0.122	0.200	-
Na^+	0.040	0.116	0.146	0.193	0.126	0.159	0.024	-
K^+	0.105	0.081	0.095	0.120	0.180	0.188	-0.050	-
Rb^+	0.120	0.075	0.078	0.090	-	0.194	-0.072	-
Cs^+	0.156	0.067	0.071	0.059	0.199	0.203	-0.088	-
Mg^{2+}	-	0.260	0.325	0.393	-	-	0.237	0.393
Ca^{2+}	-	0.224	0.278	0.339	-	-	0.124	0.332
Sr^{2+}	-	0.205	0.255	0.324	-	-	0.069	0.304
Ba^{2+}	-	0.164	0.217	0.316	-	-	-0.055	0.231
Zn^{2+}	-	0.091	0.146	0.257	-	-	0.237	0.405
Co^{2+}	-	0.239	0.318	0.399	-	-	0.221	0.393
Ni^{2+}	-	0.248	0.340	-	-	-	0.238	0.386
Cn^{2+}	-	0.147	0.228	-	-	-	0.206	0.397
Mn^{2+}	-	0.205	0.315	-	-	-	-	0.476

$$V_{s(ij)} = \frac{1}{2}V_{s(ij)}\,(\text{cation}) + V_{s(ij)}(\text{anion}) \qquad (5)$$

in case of 2:1 - electrolytes, where i is the index of cation and j - the index of anion.

One structural characteristics which represents the ion - solvent interaction in the framework of simple model given above, is the electrostatic free energy ΔG_{el} of ion in a given solvent. According to the Born model[15] this energy is

$$\Delta G_{el} = \frac{(ze)^2}{2\varepsilon r} \quad , \qquad (6)$$

where z is the ion and e the elementary charge, r denotes the ion radius and ε - the macroscopic dielectric constant of the solvent.

Actually the excellent linear dependences between the

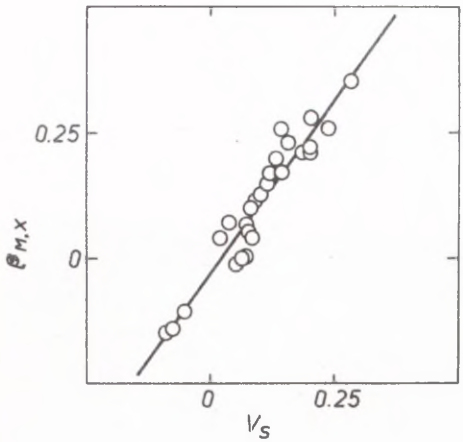

Fig. 1. The Relationship between the Guggenheim and Turgeon's[12] values for ion-solvent interaction constants β_{MX} and specific structurization volumes V_s for some 1:1 electrolytes in aqueous solutions

$V_{s(ij)}$- values and the parameters $\frac{z_i}{r_i}$ * are obtained for series of electrolytes with common anion (see Fig. 3). Remarkably enough, the crystallographic radiuses r_i of ions may be used in such correlations. The use of z instead of z^2 is caused by the difference of cation contributions in $V_{s(ij)}$- parameter of 1:1 and 2:1- electrolytes (cf. Eq. (4) and (5)). Therefore the sensitivity of $V_{s(ij)}$ towards the ΔG_{el} is transformed into common scale for different electrolyte types.

On the other hand, there is no linear relationship between the $V_{s(ij)}$ values of electrolyte series with common cation

* The difference in cationic contributions for 1:1 and 2:1-electrolytes (cf. eq.(4) and (5))is taken into aocount. Actually $V_{s(ij)} = V_{s(ij)}/z_{cat}$ and therefore there is no quadratic dependence on charge but only linear.

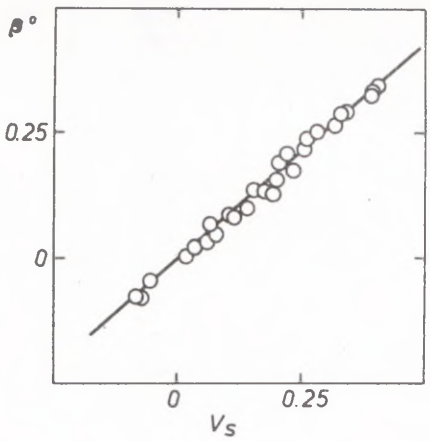

Fig. 2. The linear relationship between the ion - solvent interaction parameters β^{o} by Pitzer[14] and specific volumes V_s for some 1:1- and 2:1- electrolytes in aqueous solutions.

and the corresponding anion parameters z_j/r_j. Thus, there is a substantial unsymmetry in the ion - solvent interaction change in the electrolyte solution with the change of its concentration in respect of anions and cations. Formally, it can be presented as the "sigma-rho" type equation

$$V_{s(ij)} = V_{s(oj)} + \rho_j \sigma_i , \qquad (7)$$

where $\sigma_i = z_i/r_i$ by definition, and $V_{s(oj)}$ and ρ_j are the two specific parameters for anions. Consequently, there is one additional interaction type between the anions and solvent in comparison with cations. The parameters of linear regression treatment of the V_s data for different electrolyte series with common anion according to the equation (7) are given in Table 2. It should be noted that the cations with inert-gas structure were used in these correlations, whereas the bivalent transient metal salts reveal significant deviations in several cases and were excluded therefore. This may mean that these

transient metal cations have also an extra interaction with the solvent in comparison with simple cations.

The further analysis of anion parameters shows a linear dependence of ρ_j on the electrostatic ion - solvent interaction parameter $\rho_j = z_j/r_j$, where z_j is the charge of anion and r_j its crystallographic radius (see Fig. 4.) For the multiatomic anions the corresponding thermochemical radiuses were used. The linear relationship between ρ_j and σ_j is characterized by the linear regression parameters as follows:

$$\rho_j = (0.924 \pm 0.050) - (1.503 \pm 0.088)\,\sigma_j \qquad (8)$$

(the correlation coefficient r = 0.9903, standard deviation s = 0.057). At the same time, there is no correlation between $V_{s(oj)}$ and σ_j, and therefore the $V_{s(oj)}$ - parameter represents essentially the other type of ion - solvent interaction.

By substituting of Eq. (8) to the Eq. (7), the latter could be rewritten as follows:

$$V_{s(ij)} = V^{o}_{s(oj)} + \rho^{o}_{j}\sigma_j + \rho^{o}_{i}\sigma_i + \alpha\rho^{o}_{i}\rho^{o}_{j}\sigma_j\sigma_i \qquad (9)$$

which now comprises the additive anionic ($V^{o}_{s(oj)} + \rho^{o}_{j}\sigma_j$) and cationic ($\rho^{o}_{i}\sigma_i$) parts, and the cross-term. The sensitivity parameters ρ^{o}_{j} and ρ^{o}_{i} are universal constants for every electrolyte ($\rho^{o}_{i} = 0.924$). By taking arbitrarily $\alpha = 1$, the $\rho^{o}_{j} = -0.830$ can be found. Thus, quite interestingly the rise of electrostatic energy of ion in solvent (parameter σ) has the diametrically different effects on solvent structure around anions and cations. As far as σ has positive value for every ion, the effect of anion is that of solvent structure - breaking (negative contribution to the V_s) whereas the cations are characterized by the solvent structure - formation interaction. Due to the negative value of ρ^{o}_{j}, the cross-term is also totally negative and it is representing the structure-breaking effect, too.

The parameter $V^{o}_{s(oj)}$ is characteristic now of every individual anion. Their values are to be simply calculated according to the following formula:

Table 2

The Parameters of Linear Regression Treatment of $V_{s(ij)}^{-}$ Parameters on the Cation Electrostatic Potential Values According to the Eq. (7). For Common Anion Electrolyte series

Anion	$V_{s(oj)}$	ρ_j	r[a]	s[b]	s_o[c]	n[d]
Cl^-	-0.010 ± 0.004	0.124 ± 0.003	0.9979	0.005	0.025	9
Br^-	-0.026 ± 0.006	0.162 ± 0.004	0.9977	0.007	0.026	9
I^-	-0.038 ± 0.015	0.197 ± 0.011	0.9923	0.018	0.055	7
F^-	0.290 ± 0.026	-0.241 ± 0.033	0.9817	0.011	0.135	4
OH^-	0.288 ± 0.006	-0.148 ± 0.006	0.9985	0.005	0.039	4
CH_3COO^-	0.245 ± 0.005	-0.076 ± 0.005	0.9929	0.005	0.068	5
NO_3^-	-0.255 ± 0.005	0.272 ± 0.005	0.9994	0.005	0.020	5
ClO_4^-	-0.050 ± 0.050	0.203 ± 0.027	0.9825	0.015	0.131	4

a The correlation coefficient

b The standard deviation of linear correlation

c The normalized standard deviation ($s_o = \sqrt{\frac{s^2}{\sigma^2}}$, where σ^2 is the dispersion of the $V_{s(ij)}$ in a given series.)

d The number of cations used in correlation.

$$V^{o}_{s(oj)} = V_{s(oj)} - \rho^{o}_{j}\sigma^{-}_{j} \qquad (10)$$

and are given in Table 3. The other possible interaction between the anions An^- and solvent (water) is the hydrogen - bond formation:

$$An^- \ldots H - OH$$

The positive value of $V^{o}_{s(oj)}$ in case of every anion indicates that this effect strenghtens the water structure. The magnitude of this effect decreases markedly in the same series

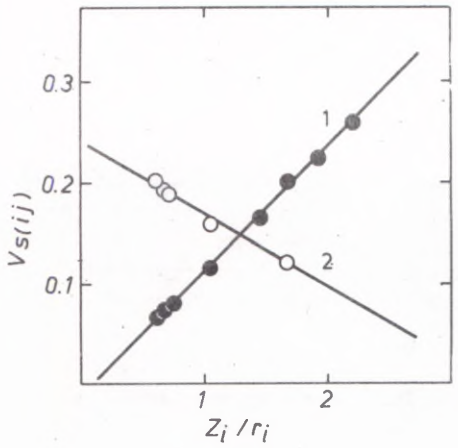

Fig. 3. The dependence of $V_{s(ij)}$ values on the cation electrostatic potential z_i/r_i in solution for some common anion electrolyte series (1-chlorides, 2-acetates).

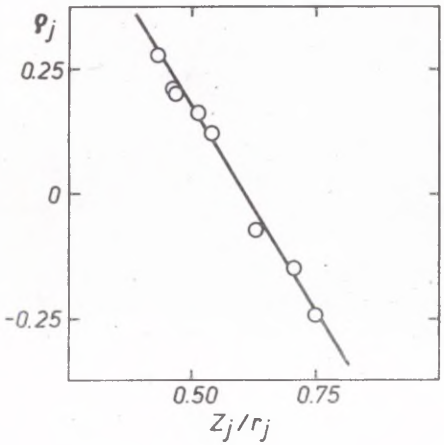

Fig. 4. The dependence of ϱ_j values for common anion electrolyte series on the anion electrostatic potential in solution z_j/r_j.

Table 3.

The $V^{o}_{s(oj)}$ - Parameters of Anions Calculated According to Equation (10).

Anion	F^-	Cl^-	Br^-	I^-	OH^-	CH_3COO^-	NO_3^-	ClO_4^-
$V^{o}_{s(oj)}$	0.914	0.449	0.398	0.348	0.877	0.717	0.098	0.338

of anions

$$OH^-,\ F^- \gg Cl^- > Br^- > I^-$$

which was obtained for the anion hydratation effects by Parker[18] from the analysis of solvolysis salt effects.

The practical importance of the analysis presented here is in the diminishing of structural parameters which determine the partial excess free energy in electrolyte solutions. Obviously instead of the $V_{s(ij)}$- parameter of every individual electrolyte we have now only one parameter for every cation (which is presented by the independent data of ionic crystallographic radiuses.), analogous set of parameters for anions (again the so-called free information) and hydrogen - bonding parameters $V^{o}_{s(oj)}$ for every anion. In addition there are two universal parameters ρ^{o}_{j} and ρ^{o}_{i}. The validity of this theoretical description can be illustrated by the comparison of the experimental $V_{s(ij)}$ values with those calculated by the use of formula (9) (cf. Fig.5.). The only salts, which do not obey Eq. (9) are the nitrates of bivalent cations.This may be caused by the specific interaction (e.g. ionic association) between the ions of these salts in aqueous solutions.

The representation of the ion - solvent interaction partial excess free energy ΔG_{is} using the $V_{s(ij)}$-parameter in form of Eq. (9) enables to estimate the individual ionic activity coefficients in the solution. We have to emphasize that this possibility is again not exactly thermodynamic[19], but depends on the extrathermodynamic relationship (7). According to the form of this equation the $V_{s(ij)}$-parameter can be divided into two parts:

$$V_{s(ij)} = V_{s(ij)}(\text{anion}) + V_{s(ij)}(\text{cation}), \qquad (11)$$

where

$$V_{s(ij)}(\text{anion}) = V_{s(oj)} + \frac{1}{2}\rho_j^o\rho_i^o\sigma_j\sigma_i , \qquad (12)$$

and

$$V_{s(ij)}(\text{cation}) = \rho_i^o\sigma_i + \frac{1}{2}\rho_i^o\rho_j^o\sigma_i\sigma_j , \qquad (13)$$

either of them is only the parameter of anion or cation, respectively. The corresponding $V_{s(ij)}$ (cation or anion) values are given in Table 4. for some electrolytes. The typical behavior of individual ion activity coefficients calculated as (cf. Eq. (2) and (3)):

$$\ln f_i = \frac{A_M z_c z_a \alpha}{2\varepsilon RT}\sqrt{c} + 2V_{s(ij)}(\text{ion}) \cdot c , \qquad (14)$$

is presented on the basis of the data for sodium chloride in Fig. 6. Starting from some critical concentration, the overall activity coefficient logarithm of cation becomes positive. For the anion the value of this quantity is always negative. It is important to notice that the activity coefficients of counterions are significantly different still in the dilute solutions.

Finally we pay attention to the treatment of the similar Guggenheim coefficients β [20] describing the ion-solvent interaction . Two parameters are given for every individual cation and anion and the average error of calculated β values was 0.006. This is comparable with the result of the present treatment. where the average error of calculated $V_{s(ij)}$ values is 0.005. However, in the present approach the number of parameters is significantly smaller and consists only one for every individual anion ($V_{s(oj)}^o$) plus two universal constants (ρ_i^o and ρ_j^o). Moreover, the parameters obtained here seem to have certain physical meaning. Therefore, the analysis of the ion - solvent interaction parameters ($V_{s(ij)}$) presented in this work seems to be superior in comparison with the earlier approaches.

Table 4.

The Individual Ion Ion-Solvent Interaction Parameters $V_{s(ij)}$ (Cation or Anion) in Aqueous Solutions at 25°C.

S a l t	$V_{s(ij)}^{(cation)}$	$V_{s(ij)}^{(anion)}$
LiCl	0.872	-0.678
NaCl	0.551	-0.432
NaBr	0.572	-0.427
NaI	0.590	-0.421
NaF	0.360	-0.323
KCl	0.393	-0.311
RbCl	0.352	-0.279
CsCl	0.317	-0.253
$MgCl_2$	1.151	-0.891
$CaCl_2$	1.006	-0.780
$CaBr_2$	1.043	-0.758
CaI_2	1.077	-0.737
$SrCl_2$	0.872	-0.677
$BaCl_2$	0.758	-0.590

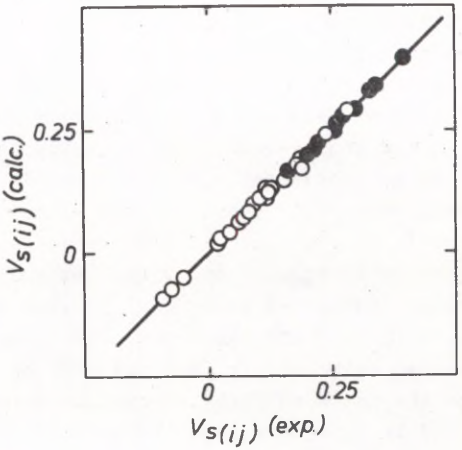

Fig.5.The Relationship between the experimental parameters $V_{s(ij)}$ and their values calculated according to Eq.(11). (1-1:1-electrolytes, 2-2:1-electrolytes)

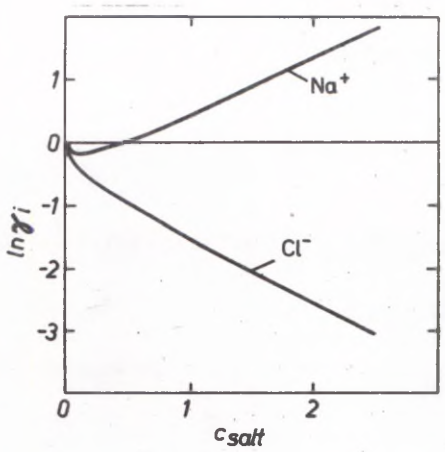

Fig. 6. The individual activity coefficient behavior of Na^+ and Cl^- - ions in aqueous solutions of NaCl according to Eq. (14)

References

1. M.M. Karelson, This journal, 21, No 1(73),160(1984)
2. M.M. Karelson and T. Sepp, This journal, 21, No 3 (75), 328(1984)
3. T. Hurlen, Acta Chem. Scand., A35, 587(1981)
4. M.M. Karelson and T. Sepp, This journal, 22, 341 (1985)
5. H.S. Frank and P.T. Thompson, J. Chem. Phys., 31,1086 (1959)
6. J.E. Desnoyers and B.E. Conway, J. Phys. Chem., 68, 2305 (1964)
7. L. Bahe, J. Phys. Chem., 76, (7), 1062 (1972)
8. R.M. Pytkowicz, K. Johnson and C. Curtis, Geochem. J., 11, 1 (1977)
9. M.M. Karelson, This journal, 22, 362 (1985)
10. K. Arakawa and K. Sasaki, Bull. Chem. Soc. Jpn., 42, (2), 303 (1969)

11. D.R. Herrick and F.H. Stillinger, J.Chem.Phys., 65,(4) 1345 (1976)
12. E.A. Guggenheim and J.C. Turgeon, Trans. Farad.Soc., 51,747(1955)
13. B.E. Conway,Compr.Treat.Electrochem., 5,111(1983)
14. K.S. Pitzer, J.Phys.Chem., 77,(3),268(1973)
15. J.O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry, vol.1., Plenum Press,New York,1970
16. Handbook of Chemistry (in Russian), Part III, "Khimija", M.-L.,1964
17. K.P. Mischenko and G.M. Poltoratsky, The Problems of The Thermodynamics and Structure of Aqueous and Non-aqueous Solutions of Electrolytes (in Russian), Khimija, Leningrad, 1968
18. A.J. Parker, Quart.Revs.Chem.Soc. (London), 15, 163(1962)
19. A.F. Vorobyev and S.I. Drakin, Russ.J.Phys.Chem., 59, 505(1985)
20. L.A. Bromley, AIChE Journal, 19,313(1973)

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PRIMARY SALT EFFECT ON ACID-BASE EQUILIBRIA

M. M. Karelson
Laboratory of Chemical Kinetics and Catalysis, Tartu State University, Tartu 202400, Estonian S.S.R.

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The formula describing the neutral electrolyte additions influence on the pK values of acid-base equilibria is obtained proceeding from the Brønsted-Bjerrum principle and the structural theory of electrolyte solutions. The verification of the validity of these formula is made on the basis of experimental data on the carboxylic acid dissociation constants. The overall agreement between the experimental results and theoretical predictions is good in a wide range of additional electrolyte concentration in the solution.

The nature of primary salt effect on the chemical kinetics and equilibria have been the target of many investigations for a long time[1-14]. The fundamental cornerstone of many approaches is the well-known Brønsted-Bjerrum principle about the use of reagent activities instead of their concentrations in the calculation of the thermodynamic rate or equilibrium constants. That is, for the chemical equilibrium.

$$A + B \rightleftarrows C \qquad (1)$$

the equilibrium constant at standard (ideal) conditions is defined as

$$K = \frac{a_C}{a_A \cdot a_B} = \frac{C_C}{C_A \cdot C_B} \cdot \frac{f_C}{f_A \cdot f_B} = K_C \frac{f_C}{f_A \cdot f_B} , \qquad (2)$$

where a_i denote the activities and c_i the concentrations of the respective particles in the solution, and f_i are their activity coefficients correspondingly. The quantity K_c is essentially a function of the constituent concentrations in the solution, but usually it is the observable parameter of the equilibrium in solution (the concentrational equilibrium constant). The crucial point in the evaluation of the equilibrium constant at standard condition (corresponding to an infinitely diluted solution) is therefore the exact estimation of the activity coefficients of equilibrium constituents.

Without any doubt in many electrolyte solutions the ion association is present in a sizable extent.[15-23] However, we restrict ourselves to only the so-called strong electrolytes, presumably completely dissociated in the solution, in the further discussion. Traditionally the various extensions of Debye-Hückel theory were used then for the calculation of activity coefficients of ionic components in solution . (cf. Ref. 9-11). Recently it has been shown by several authors[24-28] that the quasi-lattice theory is much superior in comparison with original Debye-Hückel treatment of electrostatic excess free energy of ions in the solution. In the structural theory of electrolyte solution proposed by us, the ion-solvent interactions are also taken into account in the description of non-ideality of these solutions[27]. According to this theory the partial excess free energy of electrolyte is expressed as:

$$\Delta G_{ex} = \Delta G_{ii} + \Delta G_{is} , \qquad (3)$$

where ΔG_{ii} is the purely electrostatic interionic interaction free energy and ΔG_{is} denotes the formally independent excess free energy of ion-solvent interaction. It has been shown[27] that

$$\Delta G_{ii} = \frac{A_M (z_+ e)(z_- e)}{\varepsilon \bar{l}} N_A = a_t \sqrt[3]{c}, \qquad (4)$$

where z_+, z_- and e are the cation and anion ionic charges and an elementary charge, respectively, N_A is the Avogadro number and ε the macroscopic dielectric constant of the sol-

vent at given conditions. The variable $\bar{l}$ denotes the mean distance between the nearest-neighbouring ions of the uniform distribution of particles in the volume. In the quasi-lattice theories[24-26] the parameter A_M is expected to have the meaning of the Madelung constant for the simplest lattice of the given electrolyte charge type. Recently it was shown by us[29] that this parameter can be calculated without any assumption about long-range order in solution if to use a suitable distribution function for ions along a reference ion in the original Debye-Hückel theory. Therefore the multiplier a_t before the cube-root of electrolyte in Eq. (4) concentration is a completely theoretical constant depending only on the charge type of electrolyte and solvent properties. At the standard conditions (25°C, 1 at) in water coefficient a_t has the following values:

$$a_t = -0.7961 \quad \text{for 1:1 electrolytes,} \qquad (5^a)$$

$$a_t = -2.7339 \quad \text{for 1:2 and 2:1 electrolytes} \qquad (5^b)$$

and

$$a_t = -5.2118 \quad \text{for 1:3 and 3:1 electrolytes,} \qquad (5^c)$$

The ion - solvent interaction excess free energy obeys the following equation:

$$\Delta G_{is} = 2\nu RTV_s \cdot c = b_i c \qquad (6)$$

where ν is the number of ions in electrolyte, R - the universal gas constant and T the temperature (°K). This part of excess free energy ΔG_{is} is present for the nonionic solutes in solution, too. The essential parameter determining the dependence of ΔG_{is} from the concentration c, is the characteristic volume V_s specific to every solute. In the framework of two-state theory of liquids[30] this is numerically equal to the volume around a solute (ions) in which the solvent is completely transferred into an ideally ordered structure (positive values of V_s) or a fully disordered one (negative values of V_s). Therefore the mean activity coefficient of an ion in electrolyte solution can be found as

$$f_i = \exp(\Delta G_{ex}/\nu RT) = \exp\left(\frac{a_t}{\nu RT}\sqrt[3]{c} + \frac{b_i}{\nu RT}c\right) \quad (7^a)$$

or

$$\log f_i = \frac{a_t}{2.303\nu RT}\sqrt[3]{c} + \frac{b_i}{2.303\nu RT}\cdot c = a_1\sqrt[3]{c} + a_2 c \quad (7^b)$$

where a_1 is now a universal coefficient for every electrolyte of a given charge type, and a_2 is a specific constant for an electrolyte.

The use of this result in the Brønsted-Bjerrum equation (2) enables now to account the solution non-ideality effects on the concentrational equilibrium constants between ionic reagents. For the sake of simplicity we investigate into the salt effects on univalent reagents by 1:1-electrolytes. The most thoroughly studied equilibria of this type are the acidities of the OH-acids and protonation of the substituted ammonium bases in aqueous solutions. In the following discussion the concentration of the equilibrium constituents is assumed to be negligible in comparison with the electrolyte addition concentration.

$$ROH \overset{K_a}{\rightleftharpoons} RO^- + H^+ \quad (8)$$

the constant pK_a equals:

$$pK_a = -\log\frac{c_{RO^-}\, c_{H^+}}{c_{ROH}} - \log\frac{f_{RO^-}\, f_{H^+}}{f_{ROH}} =$$

$$= pK_c - \log\frac{f_{RO^-}\, f_{H^+}}{f_{ROH}} =$$

$$= pK_c - 2a_1\sqrt[3]{c} - (a_{2(RO^-)} + a_{2(H^+)} - a_{2(ROH)})\cdot c \quad (9)$$

or otherwise

$$pK_c = pK_a + 2a_1\sqrt[3]{c} + \Delta a_2 \cdot c, \quad (10)$$

where the coefficient $\Delta a_2 = a_{2(RO^-)} + a_{2(H^+)} - a_{2(ROH)}$ is generally adjacent to the particular acid, ROH, and electrolyte in solution.

In the protonation equilibrium of ammonium bases

$$R_3NH^+ \overset{K_a}{\rightleftharpoons} R_3N + H^+ \qquad (11)$$

the constant pK_a is expressed as follows:

$$pK_a = pK_c - \log \frac{f_{R_3N^+} f_{H^+}}{f_{R_3NH^+}} =$$

$$= pK_c - (a_{2(R_3N)} + a_{2(H^+)} - a_{2(R_3NH^+)}) \cdot c \qquad (12)$$

or

$$pK_c = pK_a + \Delta a_2 \cdot c, \qquad (13)$$

where $\Delta a_2 = a_{2(R_3N)} + a_{2(H^+)} - a_{2(R_3NH^+)}$ is now a constant connected with the given base, R_3N .

The linear relationships (13) for the neutral ammonium bases were known long ago (cf. Ref. 31.-34 and Fig. 1). The connection of these relationships in wide range of electrolyte concentration with the variety of acidity functions is described elsewhere.[26] The theoretical calculation of the Δa_2 parameters which reduces to the evaluation of the specific volumes V_s for reagents adjacent in equilibrium will be also discussed in our further publications.

In this work we concentrate on the verification of the simple structural theory of electrolyte solutions on the basis of experimental salt effects on the pK_c (10) of the carboxylic acids. The latter have a characteristic nonlinear dependence on the additional electrolyte concentration (cf. Fig. 2). The results of the multilinear least-squares treatment of the numerous literature data on the pK_c values in various 1:1 salt aqueous solutions according to Eq. (10) is given in Table 1. The parameters pK_a, $2a_1$ and Δa_2 were found as the regression coefficients. The value of coefficient $2a_1$ is comparable with its theoretical value following from the structural theory of solutions:

$$2a_{1t} = -0.5587 \qquad (14)$$

The small systematical positive deviations from this value (cf. Table 1.) for most acids is due to the absence of the data for dilute solutions ($C < 0.1$ M), as it follows from

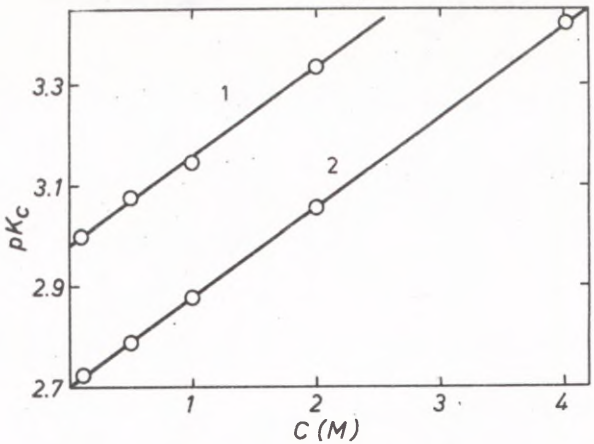
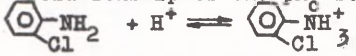


Fig.1.The linear relationship of the pK_c for the equilibrium



on the concentration of sodium chloride in aqueous solutions at 5°C (1) and 25°C (2).

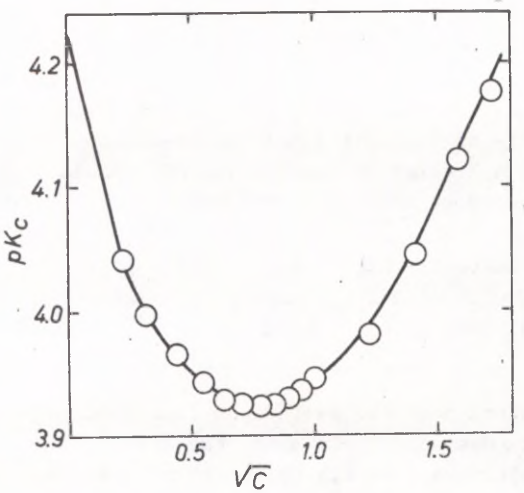


Fig.2.The dependence of the pK_c for the bensoic acid dissociation in aqueous solutions on the concentration of sodium chloride. Circles denote the experimental values[43]. The curve is calculated according to Eq. (10) (Δa_2=0.252)

Table 1

The Results of the Multilinear Least-Squares Treatment of the pK_c of Several Carboxylic Acids in Aqueous Solutions According to the (10)

No	Acid	Salt added	pK_a	$2a_1$	Δa_2	r^a	s^b	s_o^c	Ref.
1	2	3	4	5	6	7	8	9	10
1.	HCOOH	NaCl	3.771 ± 0.017	-0.545 ± 0.029	0.258 ± 0.010	0.9985	0.007	0.0025	37
		KCl	3.750 ± 0.008	-0.494 ± 0.014	0.270 ± 0.005	0.9998	0.003	0.003	37
2.	CH_3COOH	NaCl	4.782 ± 0.052	-0.550 ± 0.065	0.281 ± 0.013	0.9997	0.010	0.015	38
		NaCl	4.754 ± 0.006	-0.499 ± 0.014	0.250 ± 0.006	0.9979	0.007	0.025	39
		NaCl	4.776 ± 0.006	-0.493 ± 0.012	0.271 ± 0.004	0.9996	0.006	0.011	40
		KCl	4.742 ± 0.023	-0.474 ± 0.029	0.280 ± 0.006	0.9999	0.004	0.006	39
		KCl	4.763 ± 0.004	-0.450 ± 0.009	0.269 ± 0.004	0.9997	0.004	0.010	40
3.	C_2H_5COOH	NaCl	4.883 ± 0.013	-0.498 ± 0.014	0.256 ± 0.007	0.9993	0.005	0.017	37
4.	C_3H_7COOH	NaCl	4.822 ± 0.012	-0.501 ± 0.020	0.256 ± 0.007	0.9994	0.005	0.016	37

Table 1 continued

1	2	3	4	5	6	7	8	9	10
5.	$(CH_3)_2CHCOOH$	KCl	4.861± 0.012	-0.504± 0.021	0.267± 0.007	0.9994	0.005	0.015	37
6.	C_4H_9COOH	NaCl	4.847± 0.012	-0.528± 0.020	0.263± 0.007	0.9994	0.005	0.015	37
7.	$(CH_3)_3CCOOH$	NaCl	5.058± 0.026	-0.547± 0.044	0.246± 0.015	0.9956	0.010	0.042	37
8.	$C_5H_{11}COOH$	NaCl	4.852± 0.020	-0.506± 0.027	0.255± 0.009	0.9989	0.006	0.021	37
9.	$(CH_3)_2CH(CH_2)_2COOH$	NaCl	4.840± 0.011	-0.475± 0.019	0.247± 0.006	0.9995	0.004	0.015	37
10.	$C_6H_{13}COOH$	NaCl	4.867± 0.013	-0.515± 0.022	0.259± 0.007	0.9993	0.005	0.017	37
11.	$ClCH_2COOH$	NaCl	2.845± 0.010	-0.500± 0.017	0.235± 0.006	0.9994	0.004	0.016	41
12.	$BrCH_2COOH$	NaCl	2.884± 0.015	-0.444± 0.026	0.215± 0.008	0.9984	0.006	0.025	42
13.	ICH_2COOH	NaCl	3.166± 0.016	-0.492± 0.027	0.251± 0.009	0.9989	0.006	0.021	42
14.	$OHCH_2COOH$	NaCl	3.852± 0.014	-0.530± 0.024	0.227± 0.008	0.9982	0.006	0.027	41
15.	$Cl(CH_2)_2COOH$	NaCl	4.124± 0.011	-0.520± 0.019	0.255± 0.006	0.9994	0.004	0.016	42
16.	$Br(CH_2)_2COOH$	NaCl	4.027± 0.017	-0.532± 0.029	0.258± 0.010	0.9985	0.007	0.024	42

Table 1 continued

1	2	3	4	5	6	7	8	9	10
17.	$I(CH_2)_2COOH$	NaCl	4.096 ± 0.004	-0.507 ± 0.006	0.253 ± 0.002	0.9999	0.001	0.005	42
18.	C_6H_5COOH	NaCl	4.234 ± 0.025	-0.507 ± 0.005	0.232 ± 0.019	0.9943	0.007	0.076	43
		KCl	4.225 ± 0.002	-0.507 ± 0.004	0.243 ± 0.001	0.9999	0.001	0.004	43
19.	$C_6H_5CH_2COOH$	NaCl	4.327 ± 0.008	-0.522 ± 0.014	0.250 ± 0.005	0.9996	0.003	0.012	43
		KCl	4.322 ± 0.006	-0.505 ± 0.010	0.265 ± 0.003	0.9999	0.002	0.007	43
20.	$C_6H_5(CH_2)_2COOH$	NaCl	4.702 ± 0.005	-0.545 ± 0.009	0.265 ± 0.003	0.9999	0.002	0.008	43
		KCl	4.706 ± 0.021	-0.549 ± 0.038	0.292 ± 0.013	0.9990	0.018	0.025	43
21.	$2\text{-OH-}C_6H_4COOH$	KCl	3.068 ± 0.020	-0.538 ± 0.034	0.241 ± 0.011	0.9972	0.008	0.034	43
22.	$3\text{-OH-}C_6H_4COOH$	NaCl	4.196 ± 0.018	-0.565 ± 0.030	0.249 ± 0.009	0.9979	0.007	0.029	43
		KCl	4.193 ± 0.015	-0.538 ± 0.026	0.247 ± 0.008	0.9986	0.006	0.024	43

a) The correlation coefficient

b) The standard deviation of the correlation

c) The normalized standard deviation $s_o = \sqrt{\frac{s_o^2}{\sigma^2}}$, where σ^2 is the dispersion of the quantity to be corrected (pK_c).

Table 2

The Results of the Linear Regression Treatment of the pK_c Values of Several Carbocylic Acids in Aqueous Solutions According to Eq. (15).

No	Acid	Salt added	pK_a	Δa_2	$r^{(a}$	$s^{(b}$	$s_o^{(c}$	Ref.
1	2	3	4	5	6	7	8	9
1.	HCOOH	NaCl	3.768 ± 0.004	0.257 ± 0.002	0.9998	0.006	0.008	37
		KCl	3.776 ± 0.003	0.284 ± 0.002	0.9999	0.005	0.006	37
2.	CH_3COOH	NaCl	4.773 ± 0.007	0.279 ± 0.002	0.9999	0.009	0.008	38
		NaCl	4.779 ± 0.006	0.279 ± 0.005	0.9989	0.015	0.017	39
		NaCl	4.797 ± 0.004	0.286 ± 0.002	0.9998	0.010	0.008	40
		KCl	4.792 ± 0.005	0.293 ± 0.002	0.9999	0.006	0.005	39
		KCl	4.800 ± 0.006	0.303 ± 0.005	0.9992	0.014	0.016	40
3.	C_2H_5COOH	NaCl	4.906 ± 0.004	0.269 ± 0.002	0.9998	0.006	0.008	37
4.	C_3H_7COOH	NaCl	4.845 ± 0.004	0.268 ± 0.002	0.9998	0.006	0.007	37
5.	$(CH_3)_2CHCOOH$	NaCl	4.872 ± 0.003	0.260 ± 0.002	0.9999	0.005	0.007	37

Table 2 continued

1	2	3	4	5	6	7	8	9
6.	C_4H_9COOH	NaCl	4.853 ± 0.003	0.266 ± 0.002	0.9999	0.004	0.006	37
7.	$(CH_3)_3CCOOH$	NaCl	5.054 ± 0.006	0.244 ± 0.003	0.9995	0.009	0.013	37
8.	$C_5H_{11}COOH$	NaCl	4.886 ± 0.004	0.266 ± 0.002	0.9998	0.006	0.008	37
9.	$(CH_3)_2CH(CH_2)_2COOH$	NaCl	4.877 ± 0.004	0.268 ± 0.003	0.9997	0.007	0.009	37
10.	$C_6H_{13}COOH$	NaCl	4.881 ± 0.003	0.267 ± 0.002	0.9999	0.005	0.007	37
11.	$ClCH_2COOH$	NaCl	2.868 ± 0.003	0.247 ± 0.002	0.9998	0.005	0.007	41
12.	$BrCH_2COOH$	NaCl	2.939 ± 0.006	0.245 ± 0.004	0.9993	0.011	0.015	42
13.	ICH_2COOH	NaCl	3.193 ± 0.004	0.266 ± 0.003	0.9997	0.007	0.009	42
14.	$OHCH_2COOH$	NaCl	3.857 ± 0.003	0.230 ± 0.002	0.9998	0.005	0.008	41
15.	$Cl(CH_2)_2COOH$	NaCl	4.135 ± 0.003	0.261 ± 0.002	0.9999	0.004	0.006	42
16.	$Br(CH_2)_2COOH$	NaCl	4.031 ± 0.004	0.260 ± 0.002	0.9996	0.009	0.011	42

Table 2 continued

1	2	3	4	5	6	7	8	9
17.	$I(CH_2)_2COOH$	NaCl	$4.114^{\pm}$ 0.002	$0.264^{\pm}$ 0.001	0.9999	0.003	0.004	42
18.	C_6H_5COOH	NaCl	$4.251^{\pm}$ 0.004	$0.245^{\pm}$ 0.004	0.9996	0.006	0.017	43
		KCl	$4.242^{\pm}$ 0.002	$0.254^{\pm}$ 0.001	0.9999	0.003	0.005	43
19.	$C_6H_5CH_2COOH$	NaCl	$4.337^{\pm}$ 0.002	$0.255^{\pm}$ 0.001	0.9999	0.003	0.005	43
		KCl	$4.342^{\pm}$ 0.002	$0.276^{\pm}$ 0.001	0.9999	0.004	0.005	43
20.	$C_6H_5(CH_2)_2COOH$	NaCl	$4.699^{\pm}$ 0.001	$0.263^{\pm}$ 0.001	0.9999	0.002	0.003	43
		KCl	$4.700^{\pm}$ 0.004	$0.289^{\pm}$ 0.003	0.9998	0.007	0.010	43
21.	$2\text{-}OH\text{-}C_6H_4COOH$	KCl	$3.069^{\pm}$ 0.004	$0.241^{\pm}$ 0.002	0.9997	0.007	0.010	43
22.	$3\text{-}OH\text{-}C_6H_4COOH$	NaCl	$4.181^{\pm}$ 0.004	$0.241^{\pm}$ 0.002	0.9997	0.007	0.010	43
		KCl	$4.194^{\pm}$ 0.003	$0.247^{\pm}$ 0.002	0.9998	0.005	0.008	43

a - c cf. footnotes (a-c) at Table 1.

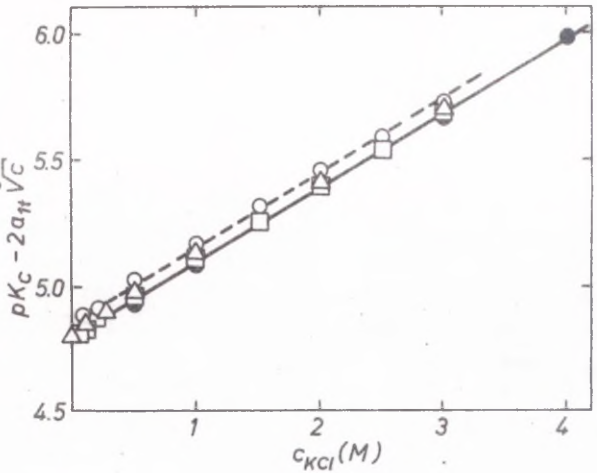


Fig.3. The linear relationship of function $pK_c - 2a_{lt}\sqrt[3]{c}$ for acetic acid in aqueous solutions at 25°C on concentration of potassium chloride.

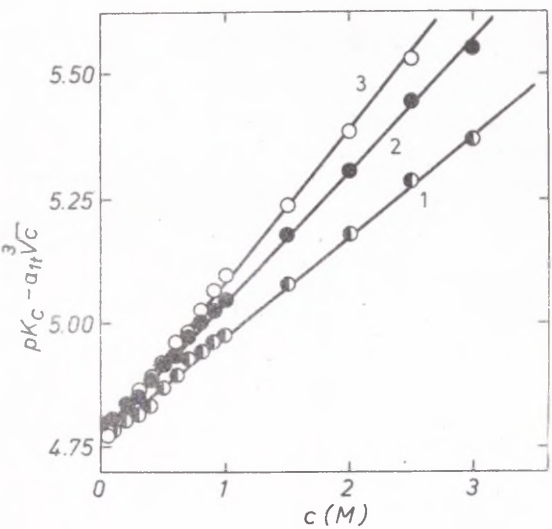


Fig.4. The linear relationship of function $pK_c - a_{lt}\sqrt[3]{c}$ for acetic acid in aqueous solutions at 25°C on the concentration of additional electrolyte (1-KCl, 2-NaCl, 3-LiCl)

the computational model experiments. Therefore to our opinion the preferred treatment of pK_c data is according to the one - parameter equation:

$$Y = pK_c - 2a_{1t}\sqrt[3]{c} = pK_a + \Delta a_2 \cdot c \quad , \qquad (15)$$

where the theoretical value of a_{1t} (14) is used in the ion electrostatic activity coefficient term substracted from the experimental pK_c value. The function which is linearly correlated with the molar concentration of additional electrolyte in the solution is Y now. An example of such relationship is given in Fig. 3. The results of the linear regression treatment of experimental data according to equation (15) is given in Table 2. It has to be mentioned that most of the statistical parameters (esp. the error of the pK_a estimate , the correlation coefficient r and the normalized standard deviation s_o) are significantly better than in the case of two- parameter treatment (10). That is why in the presence of the limited data sets the theoretical equation (15) is more justified.

Parameters Δa_2, which describe the salt influence on the nonionic excess free energy of acid - base equilibrium components, seem to be fairly independent of the acid structure at a constant salt used as an addition (cf. Table 2.) . If to recall the definition of this parameter (Eq. (6),(7) and (10)), it means that the difference of the characteristic volumes V_s for the neutral acid and carboxylate ion is practically insensitive to the structure of this acid, i.e.:

$$V_{s(RCOOH)} - V_{s(RCOO^-)} \cong \text{const.} \qquad (16)$$

Small deviations from this constancy can be observed for the acids having strongly polar substituents adjacent to the carboxylate group.However, the reality of this behaviour has to be justified with careful special investigations.

Still, different salts as the additions cause significant differences in the slopes Δa_2 (see Fig. 4) of the linearities (15). This is not unusual, because it had been shown[49] in the case of pure electrolytes themselves that V_s

is not an additive parameter of the solution constituents but includes the crossterms between the structure - formation parameters of different ingredients. The detailed analysis of the structural dependence of the Δa_2 (ΔV_s) parameters of the different chemical reactions will be discussed elsewhere on the basis of a much wider experimental material.

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References.

1. J.N. Brönsted, Z.phys.Chem., 108, 69(1922)
2. J.N. Brönsted, Z.phys.Chem., 115, 337 (1925)
3. N. Bjerrum, Z.phys.Chem., 108, 82 (1924)
4. G. Scatchard, Chem.Revs.,10, 229 (1932)
5. A.R. Olsen and T.R. Simonsen, J.Chem.Phys., 17,1167 (1949)
6. C.W. Davies and I.W. Williams, Trans. Farad. Soc., 54, 1547 (1958)
7. A. Indelli, Isr. J. Chem.,9,301 (1971)
8. V.K.LaMer and M.E. Kamner, J. Amer.Chem.Soc., 57,2662 (1935)
9. E.A. Moelwyn-Hughes, The Chemical Statics and Kinetics of Solutions. Academic Press, London, 1971
10. J.E. Gordon, The Organic Chemistry of Electrolyte Solutions, J. Wiley-Interscience Publications, New York, 1975
11. S.G. Entelis and R.P. Tiger, The Reaction Kinetics in Liquid State, Khimija, Moscow, 1973 (in Russian).
12. E.S. Rudakov, Organic Reactivity, 7,779(1970)
13. E.S. Rudakov, Dokl.AN SSSR, 275, 666 (1984)
14. V.A. Palm, T.O. Püssa, V.M. Nummert, M.M. Karelson and I.A. Koppel, Organic Reactivity, 10, 223 (1973)
15. C.W. Davies, Ion Association, Butterworths, London,1962
16. A.F. Vorobyov, "12-th Mendeleyev Meeting on Gen. and Appl. Chem.," Moscow, No 3, 171 (1981)
17. M. Eigen, Discuss.Farad.Soc., 24, 25(1957)
18. L. Blandamer, T.E. Gough, and M.C.R. Symons, Trans. Farad.Soc., 62, 269 (1966)

19. G.H. Nancollas and A.C. Park, J.Phys.Chem., 71, 3678(1967)
20. A.I. Popov, Rev. Pure Appl.Chem., 41, 275(1975)
21. D.W. James and R.L. Frost, Aust.J.Chem., 35, 1793(1982)
22. H. Yokoyama and H. Yamatera, Bull.Chem.Soc.Jpn., 54, 2286(1981)
23. G.R. Allakhverdov, Russ.J.Phys.Chem., 59, 76(1985)
24. H.S. Frank and P.T. Thomson, Ch.8 in: Structure of Electrolytic Solutions," Ed. W.J. Hamer, J.Wiley and Sons, New-York, 1959
25. I. Ruff, J. Chem.Soc.Faraday Trans., II, 73, 1858(1977)
26. T. Hurlen, Acta Chem.Scand., A35, 587 (1981)
27. M.M. Karelson, Organic Reactivity, 21, 160 (1984)
28. M.M. Karelson and T. Sepp, Organic Reactivity, 21, 328 (1984)
29. M.M. Karelson, Organic Reactivity, 22, 362 (1985)
30. K. Arakawa and K. Sasaki, Bull.Chem.Soc.Jpn., 42, (2), 303 (1969)
31. F.A. Long and D. McIntyre, J.Amer.Chem.Soc., 76, 3240 (1954)
32. M.A. Paul, J.Amer.Chem.Soc., 76, 3236 (1954)
33. A. Aboul-Seoud and M.El-Hares, Rec.Trav.Chim.Pays-Bas, 83, 1247(1964)
34. A. Aboul-Seoud and J.A.S. Mansour, Bull.Soc.Chim.Belg., 79, 617 (1970)
35. E. Chase and M. Kilpatrick, J. Amer.Chem.Soc., 53, 2589 (1931)
36. H. Kuura and M.M. Karelson, This journal, 22, 220 (1985)
37. E. Larsson and B. Adell, Z.phys.Chem., A156, 381(1931)
38. A. von Kiss and A. Urmanczy, Z.phys.Chem., A171, 257 (1935)
39. H.S. Harned and R.W. Ehlers, J.Amer.Chem.Soc., 55, 652, 2379 (1933)
40. S. Kilpi and A. Meretoja, Z.phys.Chem., A179, 371(1937)
41. E. Larsson and B. Adell, Z.phys.chem., A157, 342 (1931)
42. E. Larsson, Z. phys.Chem., A165, 53(1933)
43. T.G. Brockman and M. Kilpatrick, J.Amer.Chem.Soc., 50, 1483(1934)

4. B. Adell, Z.phys.Chem., A185, 161(1940)
5. H.S. Harned and R.W. Ehlers, J.Amer.Chem.Soc., 54, 1350(1932)
6. E. Larsson and B. Adell, Z.phys.Chem., A156,352(1931)
7. H.M. Dawson and W. Lawson, J.Chem.Soc., 1929, 1217
8. M. Kilpatrick and D. Evans, J.Amer.Chem.Soc., 75, 586 (1953)
9. M.M. Karelson, Organic Reactivity, 22, 373 (1985)

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